Enhancement of Methane Production From Anaerobic Digestion of Wastewater Treatment Sludge

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Abstract

Anaerobic digestion is a commonly used technique in treating industrial, rural effluents and sewage sludge. Methane, CH4, produced in anaerobic digestion is a valuable renewable energy source. In wastewater treatment plant (WWTP), primary and secondary sludge are produced at different stages of wastewater treatment process. They are different in terms of composition and degradability. Experiments (batch/ semi-continuous) showed that primary sludge was more degradable and produced higher methane than secondary sludge.

As primary sludge is highly degradable, the possibility of increasing feeding rate was examined. This study found that the increased in feeding rate eventually leaded to massive methanogens washout and hence digester failure. In order to maintain the stability of primary sludge reactor at shorter hydraulic retention time (HRT), a biomass recycling method was investigated. It was found that the reactor remains stable at shorter HRT (16 days). However, further investigations are required for this technique.

Secondary sludge is made up of microbial cells from secondary treatment in WWTP. Therefore, it is hydrolysis limited in anaerobic digestion due to the low degradability characteristics. To increase the hydrolysis rate of secondary sludge anaerobic digestion, two pre-treatments were examined and compared. Thermal pre-treatment increased the methane production of secondary sludge by 50% at the highest temperature (150°C), and 80°C was not found effective when treatment time is short (1 hour). However, the energy consumption of thermal pre-treatment was too high. Energy consumption was higher than the energy gained from anaerobic digestion. Hence, better heating technology is needed.

Electrolysis is an emerging technology for secondary sludge pre-treatment. It is an adaptation from the theory of water electrolysis. During electrolysis treatment, the pH of sludge changed due to the redox activity occurring at anode and cathode. The high and low pH in the anode and cathode chambers disrupted microbial cells in the sludge, and increased methane production by 30%. Energy consumption of

electrolysis was lower than the energy gained from anaerobic digestion, thus it is more energy favourable compared to thermal pre-treatment in this study.

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1 Introduction

In domestic wastewater treatment processes, raw sewage first goes through the primary sewage treatment. In the primary treatment stage, solids that are physically removed through settling from wastewater are called the primary sludge. Wastewater will then undergo the secondary treatment process called activated sludge (AS) where soluble organics are removed by microbial action. During the AS process, a proportion of the organic substances will be converted into microbial biomass. This biomass is then settled and removed as secondary sludge or waste activated sludge (WAS). Both primary and secondary sludges are then combined for further treatment. Wastewater treatment plants (WWTP) produce a large amount of sludge. The disposal of sludge is of growing importance as the process represents about 50% of the WWTP operating costs (Appels et al. 2008). Therefore, there is a need to improve the anaerobic digestion system to increase the methane production.

Anaerobic digestion is a common sludge stabilization process in wastewater treatment for the reduction of sludge volume and Chemical Oxygen Demand (COD) level before disposing into the environment (Appels et al. 2008). The by-product of anaerobic digestion, methane (CH_4), is a valuable biofuel, which can be converted into electrical energy for the treatment plant and reduces the carbon footprint of the wastewater treatment. The anaerobic digestion is a complicated process that involves anaerobic microbial metabolic activities performed by specific bacteria groups at different stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Appels et al. 2008; Geradi 2003). Among the four stages, hydrolysis is thought to be the rate-limiting step as it involves the degradation of large complex organic compounds by bacterial enzymatic action (Geradi 2003; Appels et al. 2008; Weemaes and Verstraete 1998).

1.1 Basic Principles of Anaerobic Digestion

In municipal wastewater treatment, the disposal of sludge represents up to 50% of the whole operating costs of the treatment plant (WWTP) (Appels *et al*., 2008).
With anaerobic digestion, the volume of sludge and the chemical oxygen demand (COD) level could be reduced in order to offset environmental impact when being disposed off.

Anaerobic digestion is a complex process which involve several microbial activities and depends on the suitability of environment conditions, i.e. strictly anaerobic. The processes are shown in **Figure 2-1**. There are four main stages in anaerobic digestion: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Mara and Horan 2003; Geradi 2003; Appels et al. 2008). As these four steps proceed, one could notice the intimate relationship between each subsequent stage, the degradation of substrates in each step leads to the occurrence of the next step, and different bacteria group is responsible for different stages.

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Figure 1-1. Anaerobic digestion flow chart (Appels et al. 2008).

1.1.1 Hydrolysis

In chemical terms, hydrolysis means the splitting of compound with hydro molecules (Geradi 2003). In anaerobic digestion, hydrolysis refers to the process of degradation of particulate and colloidal waste to soluble waste, which cause these simplistic molecules to be readily degraded by bacteria. In the hydrolysis process, macromolecules such as lipids, long chain fatty acids, polymeric saccharides, proteins, carbohydrates are hydrolysed by hydrolytic bacteria into monomer or dimer compounds in the form of organic acids and alcohols (Angelidaki and Sanders 2004; Mottet et al. 2009; Gavala et al. 2003).

Hydrolytic bacteria lyses cell biomass and degrade suspended organic material (SOM) either by excreting extracellular enzymes (hydrolases) into the bulk liquid, or secrete enzymes into the cell vicinity while attaching or absorb onto the particles (Angelidaki and Sanders 2004; V. A. Vavilin et al. 2008). In order for acidogens, acetogens and methanogens to be able to access to the organic materials, hydrolysis of the SOM is very important, as it reduces the size of the particles to such size where they can pass through bacterial cell walls for integrating into cell biomass as energy or nutritional sources (Kim et al. 2009).

Hydrolysis is often considered to be the rate-limiting step in anaerobic digestion, as it involves the degradation of the most complex molecules compare with those in other subsequent stages. The rate of hydrolysis can be affected by temperature and pH. The digestion temperature and pH affect the rate of hydrolysis through their combined effect on enzyme kinetics, bacterial metabolic growth and substrate solubility (Angelidaki and Sanders 2004). Besides, different hydrolases (enzymes) has different optimum pH, which will also alter the rate of hydrolysis. Nevertheless, hydrolysis is strongly dependant on the composition of the substrate. As stated in Angelidaki and Sanders (2004), the rate of hydrolysis is closely related to the physical state of the substrate and their accessibility for hydrolytic enzymes.

1.1.2 Acidogenesis and Acetogenesis

Acidogenesis is the second stage of anaerobic digestion that involves further degradation of substrates from the hydrolysis stage (Figure 1-1). This is considered the fastest process in anaerobic digestion (V. A. Vavilin et al. 2008). This process leads to the production of volatile fatty acids (VFA) associated with ammonia, carbon dioxide and hydrogen (Mara and Horan 2003; Geradi 2003).

Acetogenesis is the third stage in anaerobic digestion where acetate is formed. Degradation of organic acids (VFAs) produced from acidogenesis is the mechanisms for acetate formation. In this stage, the acids produced tend to reduce the pH in the anaerobic digester and the volatile fatty acids produced is directly proportionate to the volatile solids fed to the digester (Geradi 2003). Methanogens use acetate as their major food source in producing methane as the end product, and raise the alkalinity of the environment through producing carbon dioxide, ammonia and bicarbonate (Geradi 2003; Mara and Horan 2003; Appels et al. 2008). However, severe pH reduction can be detrimental to methanogens as they are sensitive to pHs. The optimum pH range for methanogens is between 6.5 – 8 (Mara and Horan 2003).

1.1.3 Methanogenesis

Methanogenesis is the final stage of anaerobic digestion. This is a process carried out by strict *Archea* called methanogens (Madigan and Martinko 2003). As shown in Figure 1-1, methane is produced through the degradation of simple organic compounds such as acetate, formate, methanol by methanogens (Appels et al. 2008; Geradi 2003). The rate of producing organic acids by acid-forming bacteria and the rate of acids uptake by methane-forming bacteria need to be in balance for the process not to cease due to accumulation of acids (Geradi 2003). Therefore, when VFA is produced faster than the uptake rate of methanogens, accumulation of VFA will eventually lead to the digester failing.

1.1.4 Bacteria

As anaerobic digestion is a process relying on bacterial activity, the role of bacteria is certainly important. The role of bacteria in the anaerobic digester is basically degrading and consuming the substrates, in the form of hydrolysis or reduction. It is estimated that the relative abundance of bacteria in the anaerobic digester is about 10^{16} cells per liter (Geradi, 2003). All bacteria groups in anaerobic digestion are anaerobes, and there are three main groups of bacteria: sulphate-reducing bacteria, acetate-forming bacteria and methane-forming bacteria.

1.1.4.1 Hydrolytic and Fermentative bacteria

During hydrolysis in anaerobic digestion, hydrolytic bacteria are responsible for the breakage of chemical bonds within the complex insoluble compounds. Some of the bacteria groups are capable in producing exoenzymes during hydrolysis; such as *Bacillus sp.* produces proteolytic to hydrolyze proteins, *Cellulomonas sp.* digest cellulose with saccharolytic enzyme (Geradi, 2003).

Fermentative bacteria also contribute to the degradation of insoluble organic compounds. Anaerobes undergo fermentation or anaerobic respiration to obtain energy by consuming high energy level compound and produce degraded inorganic or organic compounds as end products (Geradi, 2003; Madigan *et al.,* 2003). Facultative anaerobes and obligate anaerobes are fermentative bacteria, such as *Clostridium sp.*, *Escherichia sp., Enterobacter sp.* etc. Oxidation-reduction reaction of various organic compounds occur during fermentation, thus partially reduced organic compounds are formed, e.g. acetate, propionate, alcohol, hydrogen (Geradi, 2003). The products from fermentation vary with different fermentative bacteria. Some of the bacteria produce compounds such as acetate and hydrogen that can be used by methanogens for methane formation, whereas other products will be degraded through other biochemical pathways.

1.1.4.2 Acetate-forming bacteria (Homoacetogens)

The role of acetate-forming bacteria is important to methane production in anaerobic digestion. Homoacetogens further degrade the higher organic acids and alcohols to simple substrates mainly acetate, carbon dioxide and hydrogen (Appels *et al*., 2008). This group of bacteria, are often found to be gram-positive and from the genus *Clostridium* (Madigan *et al.*, 2003). The process for acetate formation is termed acetogenesis in anaerobic digestion. Acetate is the major 'food' source for the methanogenic bacteria, as 70% of the methane produced in the anaerobic digester is from acetate conversion, despite the higher energy gains by using hydrogen due to the limited supply of hydrogen (Geradi, 2003). Acetate-forming bacteria are only capable of producing acetate at a very low hydrogen partial pressure (Geradi, 2003).

1.1.4.3 Methane-forming bacteria

Methane-forming bacteria, or methanogens or methanogenic bacteria, are the bacteria that 'work' for the final stage of anaerobic digestion, which is called methanogenesis. They are under the Archaebacteria domain, oxygen-sensitive, fastidious, free-living terrestrial and aquatic organisms (Geradi, 2003). Methanogens are strictly anaerobes, and grow optimally in environment with oxidation-reduction potential (ORP) < -300 mV and pH at 6.5 to 7 (Appels *et al*., 2008; Geradi, 2003). They obtain energy by degrading simplistic substrates such as acetate, CO_2, H_2 or methyl group that have been breakdown in hydrolysis, acidogenesis and acetogenesis stages. Methanogenic bacteria can be categorized into three different groups depending on their energy source.

Hydrogenotrophic methanogens:

$$\mathbf{CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O}$$

$$\mathbf{4CO + 2H_2O \rightarrow CH_4 + 3CO_2}$$

Acetotrophic methanogens:

Split acetate to CO_2 and H_2, and hydrogenotrophic methanogens will then convert them into methane gas.

$$\mathbf{3CH_3COOH \rightarrow 4CO_2 + 2H_2}$$

Methylotrophic methanogens:

Grow on substrates that contain the methyl group ($-CH_3$)

$3CH_3OH + 6H_2 \rightarrow 3CH_4 + 3H_2O$

$4\,(CH_3)_3\text{-}N + 6H_2O \rightarrow 9CH_4 + 3CO_2 + 4NH_3$

(Appels *et al.*, 2008)

1.1.4.4 Sulphate-reducing bacteria

Sulphate-reducing bacteria obtain energy from reducing sulphate in the environment and they require hydrogen and acetate for multiplication, eg. *Desulfovibrio desulfuricans* (Appels *et al.*, 2008; Geradi, 2003). Thus, they are a threat to methane-forming bacteria as they are competing for the same substrates. However, the sulphate-reducing bacteria only outcompete the methanogens when the substrate-to-sulfate (COD/SO_4^{2-}) ratio is lower than 2, and methanogens will obtain hydrogen and acetate easier when the ratio is larger than 3 (Geradi, 2003). In addition, it was reported by Appels *et al.* (2008) that sulphate-reducing bacteria tend to be the dominant group at mesophilic (37^0C) condition, while methane-forming bacteria are more dominant when it is at thermophilic (55^0C).

1.2 Important control parameters for digester stability

1.2.1 pH

As methanogens are sensitive to high and low pH, the ideal range of pH for anaerobic digester to process properly will be pH 6.5 – 8 (Mara and Horan 2003). The production of excess VFAs will cause the pH to drop in the digester, thus it is often used as a control parameter for anaerobic digesters (Geradi 2003; Ahring, Sandberg, and Angelidaki 1995). However, pH is often not enough to detect the overloading of anaerobic digester due to the masking of the bicarbonate buffering in the digester (Carnaje 1995).

1.2.2 VFA

VFA concentration serves as a good indicator for digester stability. The concentration of VFAs is very important to the operation performance of anaerobic digester. As stated in Ahring, Sandberg, and Angelidaki (1995), the accumulation of VFAs reflects a kinetic instability between acid producers (acidogens or acetogens) and consumers (methanogens). VFA accumulation is often a sign of digester overloading. The concentration of the major three VFA are the most common parameter used for operational controlling, i.e. acetate, propionate and butyrate (Buyukkamaci and Filibeli 2004). It was reported that VFA below 50 mM can increase the methane production rate, and there is a slight decrease in gas production when propionate is at 100 mM (Ahring, Sandberg, and Angelidaki 1995). However, the threshold level of VFA may be different for different reactor systems.

1.2.3 Hydrogen partial pressure

In a stable anaerobic digestion process, the reduction of pH caused by VFA and hydrogen is usually neutralized the alkaline produced by methanogens in the form of bicarbonate and ammonia (Appels et al. 2008; Pullammanappallil et al. 2001). Hydrogen and acetate are the main food source for methanogens to produce methane gas. However, at high concentration of dissolved hydrogen, the conversion of long chain VFA to acetate is inhibited. As the proton (H^+) increased in the anaerobic digester, it affects the chemistry pathway of certain substrates degradation. At high concentration of dissolved hydrogen, the activity of obligate hydrogen-producing acetogens (OHPA), which convert propionate and butyrate into acetate, hydrogen and carbon dioxide, is inhibited (Mara and Horan 2003). Partial pressure of hydrogen needs to be below 10 Pa in order to maintain the syntrophic relationship between OHPA and hydrogen utilizing methanogens in anaerobic digestion (Mara and Horan 2003). The partial pressure of hydrogen in the reactor is a good parameter for monitoring the stability of the reactor.

1.2.4 Hydraulic Retention Time (HRT) and Solid Retention Time (SRT)

The solid retention time (SRT) is the average time bacteria (solids) stay in the digester, while hydraulic retention time (HRT) is the time of the wastewater or sludge is in the anaerobic digester (Appels et al. 2008; Geradi 2003). In the conventional anaerobic digester, where the volume of feed equals to the volume of effluent, HRT is same as the SRT.

When HRT and SRT are short, it imposes the risk of bacterial washout and digester instability. A fraction of bacterial population is loss each time a part of sludge is withdrawn (Appels et al. 2008). SRT less than 10 day is not recommended, as the slow-growing methanogens will not be able to compensate the loss biomass (Nges and Jing Liu 2010; Geradi 2003). Therefore, high SRT is more advantageous for anaerobic digesters. In high rate digester systems such as upflow anaerobic sludge blanket (UASB) and two-phased anaerobic digesters, the SRT is well maintained longer than HRT to ensure high biomass density in the digester (Mara and Horan 2003).

1.2.5 Mixing intensities

Mixing is important in anaerobic digestion. Adequate mixing may enhance the contact between the organic matter and the microorganisms and hence improves reactor performance (Mara and Horan 2003). It is also important for the uniform distribution of acids (e.g. VFAs) in the reactor to prevent stratification and incomplete digestion of organic matter. It was reported in Lanting (2003), high mixing intensities encourage particle size reduction and diffusion of organic substrates, which increased the working capacity of the digester. But high mixing intensity may inhibit methanogenic activity, and resulted in poor anaerobic digester performance (Mara and Horan 2003).

1.3 Pre-treatment methods

Pre-treatment of anaerobic digestion, the process before starting anaerobic digestion is where the sludges are treated chemically, mechanically or biologically. The purpose of pre-treatment is to increase the hydrolysis rate of sludge, so that more hydrolyzed products are available to the anaerobes for their metabolic activity. There have been many studies done on improving the hydrolysis with various pre-treatment methods, such as thermal pre-treatment, ultrasonic cell disruption, high pressure homogenizer etc. (Appels et al. 2008; Ge, Jensen, and Batstone 2010; Mottet et al. 2009; Weemaes and Verstraete 1998).

Different methods with different approaches would have different effects on the anaerobic digestion, and their requirements and energy consumption will also vary. Therefore, in the following discussion, various pre-treatment methods will be introduced. Although there are many types of pre-treatment available, two pre-treatments were studied in this study due to time limitations. Investigations on thermal and electrolysis pre-treatments will be carried out in this thesis, and their energy efficiency will also be compared (see chapter 3.5).

1.3.1 Thermal Pre-treatment

Thermal pre-treatment of sludge is one of the most commonly used pre-treatment methods for anaerobic digestion. It was originally being used for improving dewaterability of sludge and for producing a carbon source for denitrification in wastewater treatment (Weemaes and Verstraete 1998). Heating up sludge generally breaks down the chemical bonds of cell wall and membrane, and causes cell lysis to occur which can favor the release of organic components in hydrolysis.

An overview of thermal pre-treatment studies was reported by (Appels et al. 2008), where most of the treatments were done around 100-200^{0}C and most of the contact times tested were between 30 to 60 minutes (**Figure** 1-2). Effective temperature for thermal pre-treatment could range from 60°C to 200°C, depending on the characteristics of the sludge and also the contact time of the thermal treatment (Appels et al. 2008; Gavala et al. 2003; Valo, Carrere, and Delgenes 2004; Weemaes

and Verstraete 1998; Wilson and Novak 2009). Some studies found that thermal treatment above 220°C had a detrimental effect on methane production, due to the 'burnt sugar' effect, where they solubilisation of carbohydrates reduces at temperature above 220°C (Mottet et al. 2009; Wilson and Novak 2009).

In the mesophilic and thermophilic pre-treatment study done by (Gavala et al. 2003), both primary and secondary (activated sludge) were separated to observe response of the individual sludges to the thermal treatment. Both primary and secondary sludges were pre-treated at 70°C, and mesophilic and thermophilic anaerobic digestion were performed. The results showed that after the 70°C pre-treatment, both mesophilic and thermophilic digestion of secondary sludge have significant improvement in methane production rate, with 43-145% and 4-58% increase respectively (Gavala et al. 2003).

A study of temperature-phased anaerobic digestion system was carried out by (Ge, Jensen, and Batstone 2010), in the study, primary sludge undergone thermal pre-treatment at 50-70°C for several days and followed by mesophilic anaerobic digestion. Despite the long pre-treatment duration, the experiment only achieved 20% higher volatile solids (VS) destruction and 25% increase in methane production. It concluded that there was no improvement in VS destruction and methane production found at any increased thermophilic pre-treatment temperature above 50°C (Ge, Jensen, and Batstone 2010). This is contradictory to the previous studies mentioned, which concluded that 70°C or 165°C is effective for hydrolysis treatment (Gavala et al. 2003; Mottet et al. 2009). Nevertheless, as the studies used different source of sludge and the treatment time tested were different, it is hard to compare these studies.

Due to the differences between primary and activated sludges, the effectiveness of any pre-treatments may be different for both sludges. This suggestion agrees with the conclusion made by (Gavala et al. 2003) regarding thermal pre-treatment, where the origin of sludge is most important and will determine the effectiveness of thermal hydrolysis.

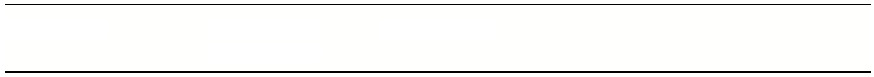

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Figure 1-2 Overview of thermal pre-treatment studies (Appels *et al.*, 2008)

1.3.2 Chemical disintegration

Chemical pre-treatment for enhancing cell destruction usually involves addition of alkaline or other chemicals to solubilise the sludge cells. Strong acids (H_2SO_4) and base (NaOH, KOH) are usually used in the acid/alkaline disintegration studies (Ge, Jensen, and Batstone 2010). Some of the studies combined thermal and acid/alkaline treatment to reduce the energy input required for heating. There are more studies available on alkaline treament compared to acid pre-treatment. This may be due to the less effectiveness of acid pre-treatment. In a thermo-chemical study done by (X. Liu

et al. 2008), thermo-acid pre-treatment showed little effect (15%) on improving VS disintegration, but thermo-alkaline showed significant increase (60%) in the VS destruction. Similar results was reported by (Valo, Carrere, and Delgenes 2004), where VS destruction increased to 30% when the pH of sludge is 12, and the effect doubled when combined the treatment with 130°C heating. These findings support the effectiveness of alkaline treatments. However, chemical treatment may be inefficient, as it requires additional chemical to neutralize the sludge back to neutral pH due to the pH sensitive methanogens (Appels et al. 2008). The additional cost of chemical reagents added and high-energy consumption of combined heating make this pre-treatment impractical to implement in WWTP (Andreottola and Foladori 2006).

Another chemical pre-treatment method, the Fenton process, also suffers the same limitation as alkaline thermal treatment. Fenton process involves addition of the Fenton's reagent (Fe (II) ion and H_2O_2), where highly reactive hydroxyl radicals are produced to decompose organic substances via oxidation. In the study done by (Erden and Filibeli 2010), the Fenton process has shown 1.2-1.4 times higher methane production. However, the high cost of the chemicals may not be higher than the profit gained from methane production.

1.3.3 Electrolysis

Electrolysis is an emerging technique for the pre-treatments in anaerobic digestion. This method is an adaption of the electrolysis of water, where water molecules are split into hydrogen and oxygen gas through redox activity. In the electrolysis process, oxidation occurs at anode, producing oxygen and leaving the proton ion (H^+) behind; reduction occurs at cathode, producing hydrogen gas and leaving hydroxide behind in the solution. This creates a pH gradient across the electrodes, where the area near anode becomes acidic, and area near cathode will turn alkaline. Electrolysis of water molecules requires a minimum voltage supply of 1.23 V at 25°C to occur (Teschke 1982).

Based on the theory of electrolysis, electrolysis pre-treatment for sludge is proposed. Equal volume of sludge is separated by ion-exchange membrane into two chambers; the pH of the two sides will eventually change due to the electrolysis of water

molecules. As the water content is high in the raw secondary sludge (before thickening), it is suitable for this study.

When the pH drops/increases, an effect similar to chemical disintegration occurs. This study proposed that electrolysis of sludge could imitate the effect of acid/alkaline pre-treatment. And when the sludges are mixed after the treatment, a neutral pH could be obtained without adding other chemical reagents. A study done by (Li-jie Song et al. 2010) demonstrated the use of electrolysis is able to increase VS destruction. The study was done in a single cell compartment, which excludes the effect of pH changes on sludge disintegration. However, the mechanisms for the electrolysis of cell membrane are unclear (Li-jie Song et al. 2010).

Although studies about electrolyzing sludge are scarce, it is worthwhile investigating the potential effects of this technique. In this study, electrolysis of secondary sludge will be examined. The pH effect will be compared with that of chemical pre-treatment (acid/alkaline). The effectiveness of these pre-treatment for increasing methane production will be discussed.

1.4 Wastewater Treatment Sludge

Currently in WaterCorp Woodman Point WWTP, primary and secondary sludge are combined together for anaerobic digestion. The current anaerobic digestion system is not able to cope up with the increasing demand in wastewater treatment, which requires construction of extra digesters. In order to reduce the cost of wastewater treatment process, a better anaerobic digestion system is required to produce more methane (biofuel) for energy cost recovery.

Primary and secondary sludge are produced in different stages of wastewater treatment process. The degradability of sludge differs with their composition. Secondary sludge is commonly accepted to be hydrolysis limited, as microbial cells are hard to degrade. In comparison, primary sludge is more readily degradable. At Woodman Point WWTP, primary and secondary sludge are run at 20 days HRT. It is proposed by this study that the HRT of primary sludge could be reduced, while

secondary sludge will need pre-treatment, as it is hydrolysis limited in anaerobic digestion.

Based on the assumption above, the feeding rate of primary sludge anaerobic digestion could be faster, and hence increase the operational capacity of the digester. On the other hand, improvement in methane production of secondary sludge anaerobic digestion may require pre-treatments to increase the hydrolysis rate. Therefore, examination of thermal and electrolysis pre-treatment will be carried out and compare.

1.5 Aims and Objectives

The main objective of this study is to enhance the methane production from anaerobic digestion of wastewater treatment sludge.

The specific aims are listed as below:

- To investigate the limiting step of anaerobic digestion of primary and secondary sludge, and evaluate appropriate approaches to each of them.
- To investigate the difference between primary and secondary sludge in terms of their methane production rate, VS destruction (%) etc.
- To investigate and compare the stability of anaerobic reactor at normal HRT (20 days) and shorter HRT (16 days). Evaluate the possibility of increasing feeding rate for primary sludge anaerobic digestion.
- To investigate the effectiveness of two pre-treatments (thermal, electrolysis) for secondary sludge anaerobic digestion.
- To compare the effectiveness of electrolysis and chemical treatment.
- To compare the energy conversion of pre-treated secondary sludge.

2 Materials and methods:

2.1 Sludge sample

Primary and secondary sludges were collected from WaterCorp Woodman point wastewater treatment plant on 1-4-2010. Sludges were stored at 4°C before using.

2.2 Experimental set up

2.2.1 Batch anaerobic digestion

Batch anaerobic digestion experiments were carried out in glass serum vials, 30 ml of anaerobic digested sludge was used as inoculum for each bottle, and the serum vials were purged with N_2/CO_2 gas to flush out oxygen from the bottles. The bottles were then sealed with butyl stoppers and aluminum caps. These were then placed in 37°C water bath, and the biogas production of each bottle was measure with the 50ml glass syringe. As the digested sludge collected from the wastewater treatment was not fully digested, it would affect the methane production measurement as it is also producing biogas. Therefore, the digested sludges were left in the hot water bath for few days until biogas production ceased. This was done to prevent the biogas produced from the anaerobic digested sludge from blurring the biogas measurement for primary and secondary sludge.

The information obtained from the VS analysis was used to calculate the volume of equal amount of VS content for all sludges. The serum bottles were opened and 20ml of feeds were put into the bottles with a known volume of sludge and de-oxygenated water (Table 1). Triplicates were prepared for the three different sludges and two bottles of digested sludge were used as controls. The controls were added with 20ml of de-oxygenated H_2O. The bottles were purged with N_2/CO_2 gas and sealed with butyl stoppers and aluminum caps, and were placed in 37°C water bath.

The biogas production and methane percentage of each bottle were measure daily. The percentage of methane from the biogas produced was measured by Gas chromatography (GC).

2.2.1 Semi-continuous lab-scale anaerobic digestion

Two 1 L anaerobic digesters were filled with 800mL of sludge leaving 200ml of air space. In this study, two reactors have been set up for different sludge feeding (primary and secondary). The digesters were 'starved' for two weeks before feeding to prevent results from blurring by biogas production from the digested sludge. Feeding of sludge was done once a day. The feeding and drawing of sludge were done at the same time. Feeding tube is longer than the extraction tube, so that the feed could be transferred to the bottom and the digested sludge of the top sludge would be removed, avoiding extraction of the incoming feed.

2.3 Data and sample collection/preparation

The conditions of the reactors were observed and controlled through the computer program LabView 8.0 (National Instruments); the measurement of pH probe will be sent to the connected computer. Temperature and stirring of digesters were controlled electronically, and the feed and decant pump are automated by the computer program. Gas production from the reactor was measured through downward displacement of oil (Dow Corning200 Fluid 50 CS).

All extracted sludges were refrigerated for analyses. For VFA analysis, extracted sludges were centrifuged at 12000 rpm for 25 minutes and only supernatant was used. The VFA samples were prepared with 10% of sludge supernatant, 10% of formic acid (10%v/v) and 80% of deionised water, in a total volume of 1 or 1.5 mL.

2.4 Analysis

2.4.1.1 Total Solids (TS) and Volatile Solids (VS) Analysis

TS and VS analysis were conducted according to Standard Methods 21st ed. (ALPHA, 1998). Prior to the methane experiment, the TS and VS concentration of the sludges was examined. Volatile solid content represents the organic component in the sludge. 10 ml of primary, secondary and mixed sludge were taken out from the sludge

samples and put into the dried crucibles, and put into oven of 105°C for overnight. After taken out from the oven, the crucibles were put into the dessicator for them to cool down before weighing. The dry mass of the solids is the TS of the sample. After the crucibles have been weighed, they were sent into the 550°C oven, where all volatile solids would be removed. The weighing procedures were repeated the same as before. VS is the weight difference between the weight of the remains in the crucible and TS.

2.4.1.2 VS destruction and VS solubilisation

VS solubilisation (%) for pre-treatments are calculated according to the following equation

$\mathbf{S_x\ (\%) = (S_t - S_u) / VS * 100}$ (Mottet et al. 2009)

Where $\mathbf{S_x}$ is the solubilisation of COD or VS; $\mathbf{S_t}$ and $\mathbf{S_u}$ are the soluble fraction (SCOD, soluble VS) in treated and untreated sludge, respectively; **VS** is the particulate fraction of untreated sludge.

VS destruction (%) of batch anaerobic digestion system is calculated based on the loss of VS in the feed sludge.

$\mathbf{VS\ destruction\ (\%) = (VS_{in} - VS_f) / VS_{in} * 100}$

VS_f = Total VS in serum vial after anaerobic digestion (g) – VS of inoculum (g)

Where VS_{in} is the volatile solid of feed added (gram), VS_f is the remaining volatile solid of feed (gram).

VS destruction (%) of semi-continuous anaerobic digestion system is calculated according to Van Kleeck equation (Switzenbaum, Farrell, and Pincince 2003).

$\mathbf{VS\ destruction\ (\%) = (VSF_i - VSF_e) / [VSF_i - (VSF_i - VSF_e)]}$

$\mathbf{VSF_i}$ is the volatile solid fraction (VS/TS) of the influent sludge and $\mathbf{VSF_e}$ is the VS fraction of effluent sludge.

2.4.2 Biogas Composition

Gas composition of serum vial tests was determined using a Varian Star 3400 GC and peak area of the thermal conductivity detector (TCD) output signal was computed via

integration using STAR Chromatography Software (© 1987–1995). 50µL gas samples were manually injected onto an Alltech 2m stainless steal Porapak Q (80/100) packed column (0.183m x 3.175mm) using a Hamilton 100µL gas tight syringe. The injector, oven, detector and filament temperatures were set at 120, 40, 120 and 170°C respectively. The N_2 carrier and reference gas flows were set to 30mL/min. Peak area for CO_2 and CH_4 standards (0, 20, 40 and 80 % (v/v)) were used to construct a standard curve, which was used for concentration determination.

2.4.3 Volatile Fatty Acids (VFAs)

A Varian Star 3400 gas chromatograph (GC) fitted with a Varian 8100 auto-sampler was used to analyse the VFA concentration of samples. Samples were first centrifuged at 12,000 rpm. The clear supernatants were then acidified with formic acid (to 1% (v/v)) before 1µL samples were injected onto an Alltech ECONOCAP^{TM} EC^{TM} 1000 (15m x 0.53mm 1.2µm i.d.) column. The carrier gas (N_2) was set at a flow rate of 30mL/min. The oven temperature was programmed as follows: initial temperature 80°C; temperature ramp 40°C/min to 140°C, hold for 1 min; temperature ramp 50°C/min to 230°C hold for 2 min. Injector and detector temperatures were set at 200 and 250°C respectively. The peak area of the Flame Ionisation Detector (FID) output signal was computed via integration using STAR Chromatography Software (© 1987-1995).

2.4.4 Pre-treatments

2.4.4.1 Thermal Pre-treatment

Secondary sludge was treated at 80°C, 100°C, 120°C and 150°C. At each temperature, 100mL of secondary sludge was autoclaved for 1 hour (Babich Maintenance & Steriliser Services, Model no. SW Hart Pan Filled). The thermal treated sludge was stored at 4°C until use to prevent bacterial activity.

2.4.4.2 Electrolysis Pre-treatment

Electrolysis pre-treatment was carried out in two merging plastic chambers, separated with anion exchange membrane (Membranes International Inc. AM7001S, Gel polystyrene cross linked with divinylbenzene; 0.45 mm thickness; electrical resistance < 40 $\Omega.cm^2$). In each chamber, 400 mL of sludge was added. Graphite sticks (graphite pencils) and graphite fabric were used as the electrode; graphite fabric was used to increase the contact area of electrode. Five graphite sticks were connected with graphite fabric (20 cm x 6 cm). Voltage supplied was 12 V, and a 5 Ω resistance was used to measure the current (A) of the system. The pH of each chamber was measured with pH probe every one hour. The experiment was operated for 30 hours (until pH turns stable), and sample was taken from each chamber during operation for COD measurement.

2.4.4.3 Chemical Treatment

The chemical reagent used in this experiment is HCl (1 M) and NaOH (0.1 M). 400mL of secondary sludge in each beaker was added with acids/alkaline until the pH is same as that of the electrolysis chamber. Acids/alkaline was added into the sludge every time there was a change in the anode/cathode chamber. Acids/alkaline pre-treated secondary sludge was neutralized to around pH 7 before feeding into serum vials.

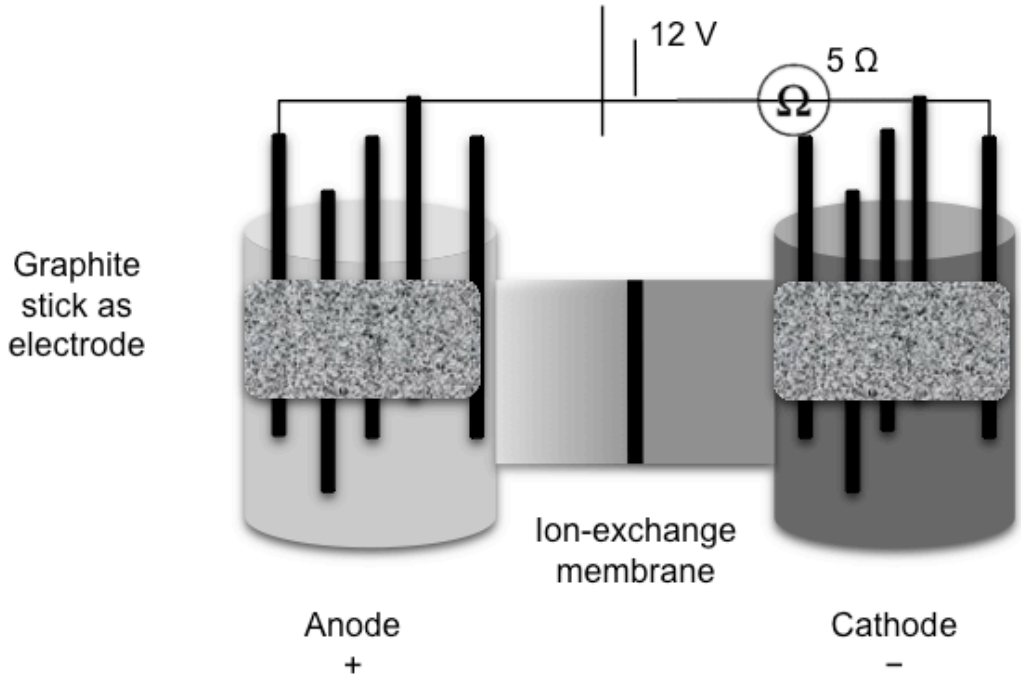

Figure 2-1 Experimental set up for electrolysis pre-treatment.

3 Results and Discussion:

3.1 Batch anaerobic digestion of primary and secondary wastewater treatment sludge

3.1.1 Introduction

Primary and secondary sludge are produced from different stages of wastewater treatment in WWTP. Thus, the characteristics of primary and secondary sludge are very different in terms of their composition (Table 3-1). The difference in their composition results in different degradability (Mara and Horan 2003; Gavala et al. 2003; Wilson and Novak 2009). Primary sludge generally consists of readily biodegradable materials, therefore easier to digest compared to secondary sludge which contains mainly biomass of microorganisms (Appels et al. 2008; Mara and Horan 2003). In most of the conventional anaerobic digestion system, primary and secondary sludge are processed together in one reactor. Due to the presence of secondary sludge, the hydraulic retention time (HRT) of the conventional anaerobic digestion system usually takes 20-30 days (Weemaes and Verstraete 1998; Appels et al. 2008).

Table 3-1 Characteristics of primary and secondary sludges from Woodman Point WWTP.

Characteristic	Primary sludge	Secondary sludge
Total solids (TS g/L)	31.42	19.19
Volatile solids (VS g/L)	28.05	16.01
Total COD (g/L)	44.98	30.94
Dissolved COD (g/L)	3.78	0.05
Carbohydrate (%TS)	34.9	49.6
Protein (%TS)	39	26.6
Fat (%TS)	11.2	5.2

The purpose of this study was to evaluate suitable treatments for both primary and secondary sludge to improve their anaerobic digestion (i.e. higher methane production). As the degradation of primary and secondary sludge is different, the treatment approach required for each of the sludge may be different. In this

experiment, primary and secondary sludge were examined for their methane production potential and bio-degradability (VS destruction) using batch anaerobic digestion under mesophilic conditions. Details of methods and material for this experiment are described in **Section** 2.2.1.

1.1.1 Methane/Biogas production

Cumulative methane production in Figure 3-1 shows that primary sludge produced more methane gas than secondary sludge at mesophilic condition (Figure 3-1). Primary sludge produced 295. 87mL of CH_4 per g VS , while secondary sludge only produced 225.22mL of CH_4 per g VS. This accounted for about 24% more methane per gram of VS was produced from primary sludge compare to secondary sludge. The difference between primary and secondary sludge in methane production in this experiment was relatively small compared to the results obtained by (Gavala et al. 2003), where the primary sludge produced 150% more methane gas than secondary sludge. This may due to the different characteristics of the sludges.

Rapid methane production was observed from both sludges (Figure 3-2). Primary sludge reached its peak production on day two, where 65.04 ml/VS g of methane was produced, while secondary sludge reached its maximum production rate on day one, where 50.88 ml/VS g of methane was produced. The methane production of both sludges reached a plateau around day 6 (Figure 3-1), where approximately 80% of the total accumulated methane gas was produced. This result imply that long HRT of 20 days as generally practiced may not be essential.

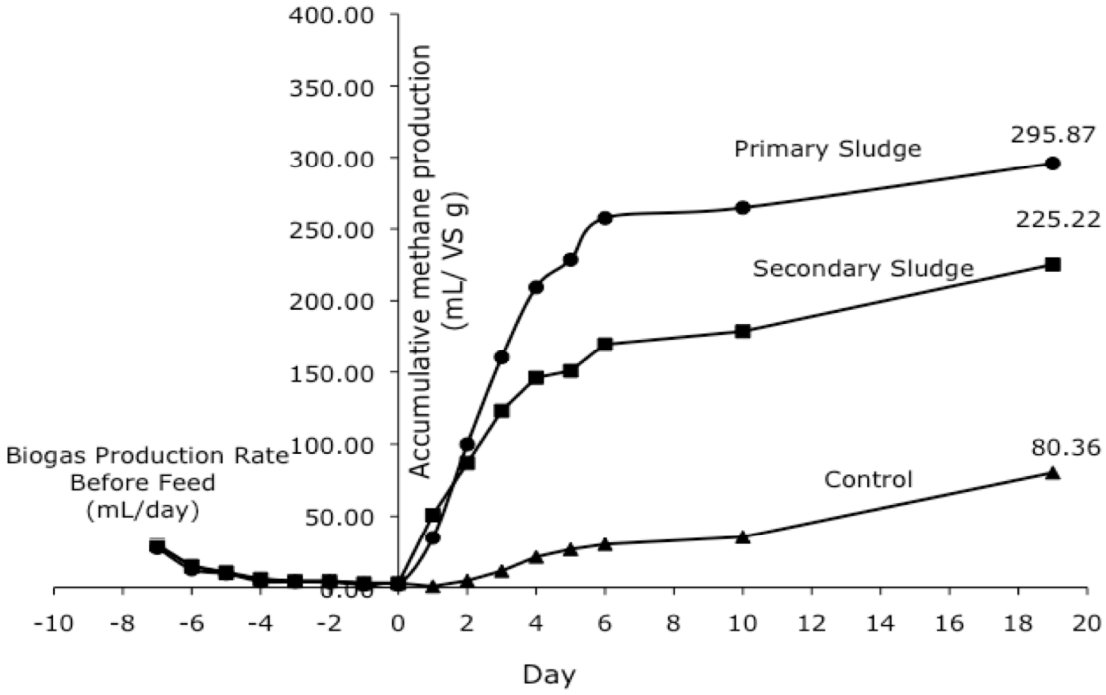

Figure 3-1 Accumulative methane production (mL/day) of primary sludge (•) and secondary sludge (▪) observed in serum vials at 37 °C. Feeding start from day 0, gas produced on negative days is the biogas production rate before feed (mL/day) of the inoculum (digested sludge) before feed. Control (▲) is fed with de-oxygenized water.

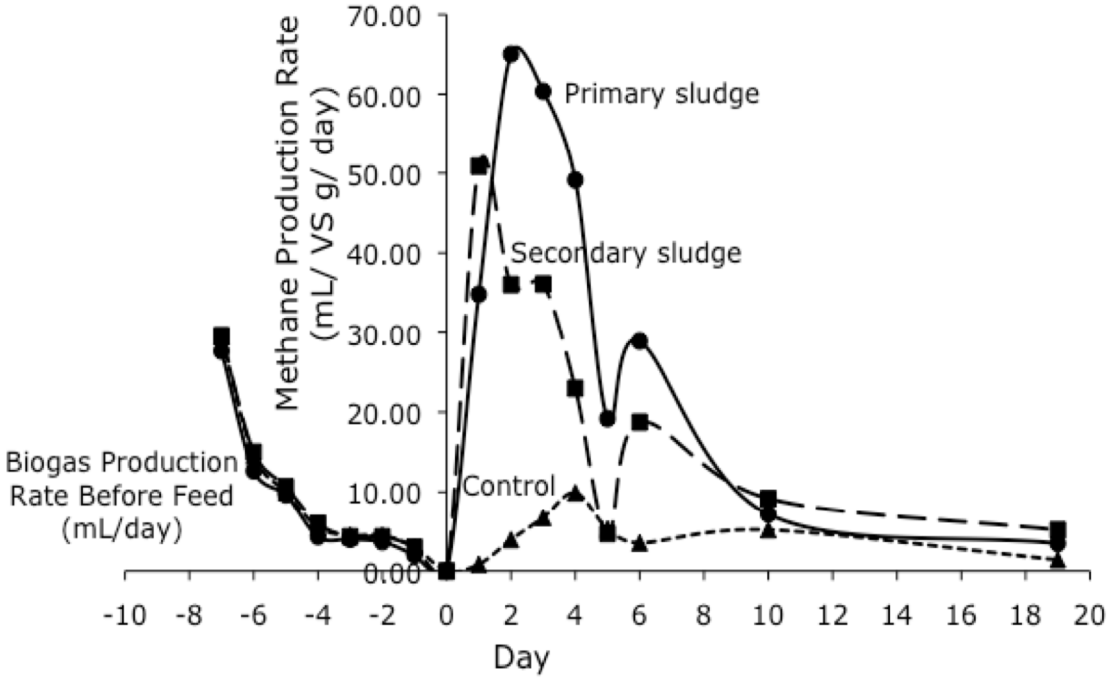

Figure 3-2 Methane production rate (mL / VS g/ day) of primary (●) and secondary sludge (■). Feeding started on day 0, gas produced on negative days is biogas production of inoculum (digested sludge) before feeding. Control (▲) is fed with de-oxygenised water.

1.1.2 VS destruction

The %VS destruction of primary and secondary sludge was calculated by estimating the loss volatile solids of feed during anaerobic digestion in the serum vials. Based on 0.3g of VS added (Table 3-2), 96% of organic content in primary sludge was digested. Secondary sludge showed only 64% of VS reduction after the anaerobic digestion.

The lower VS destruction of secondary sludge is somewhat similar to the lower methane production shown in (Figure 3-1). The results suggest that while most VS in primary sludge can be readily converted to biogas through mesospheric anaerobic digestion and only two third of secondary sludge (biomass of microorganism) is readily anaerobically biodegradable. To maximize methane production from secondary sludge, it may be essential to pre-treat the secondary sludge prior to anaerobic digestion.

Table 3-2 VS (g) and VS destruction (%) of primary and secondary sludge in serum vials before and after anaerobic digestion (AD).

VS (g) in serum vials	*Before AD (VS g)*	*After AD (VS g)*	*VS reduction (%)*
Primary	0.30	0.01	96.06
Secondary	0.30	0.17	43.68

3.2 Semi-continuous (fill and draw) anaerobic digestion of primary and secondary sludge

In the previous batch serum vials experiments, it was observed that primary sludge produced about 24% more methane gas as compared to secondary sludge at the same organic load (refer to **Section** 3.1.1). To evaluate if the same result could be obtained in a continuous system, a fill and draw anaerobic digestion was set up. The HRT was set at 20 days. This is to be consistent with current operation of anaerobic digestion at Woodman Point WWTP. Details of operation including feed characteristic are fully described in **Section** 2.2.1.

3.2.1 Biogas Production

In the semi-continuous feeding system, primary sludge reactor produced approximately 70% more biogas than secondary sludge reactor at the same HRT (**Figure 3-3**). The average biogas production of primary sludge was 0.39 L/L/day, while secondary sludge only produced 0.23 L/L/day (**Figure 3-3**). The methane concentration of biogas for both reactors ranges between 48 – 59%. Although biogas production from both reactors was much lower than that of the full scale digester at Woodman point WWTP (around 1 L/L/day), the organic content (VS) of the feed that goes into the full-scale digester (53 g/L) is nearly twice higher than that of the primary sludge (28 g/L) and three times higher than the VS of secondary sludge (16g/L).

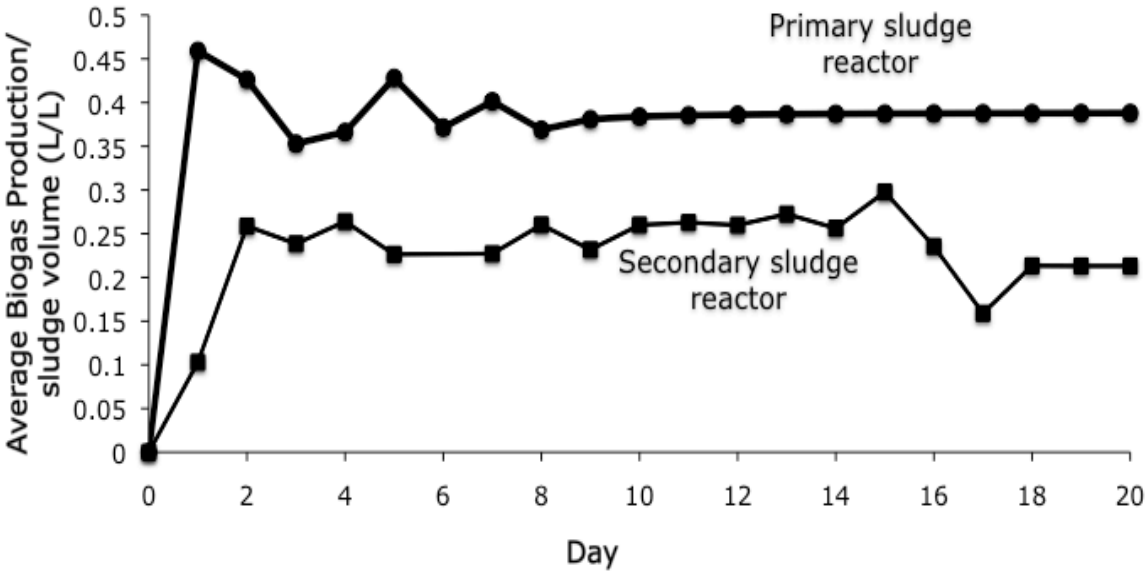

Figure 3-3 Biogas production of primary (●) and secondary sludge (■) (L/L/day) in semi-continuous feeding system.

Due to different concentration of VS between primary and secondary sludge (Table 3-1), when comparing the biogas production per organic load (gm VS fed), primary and secondary sludge did not show significant difference in their biogas production (**Figure 3-4**).

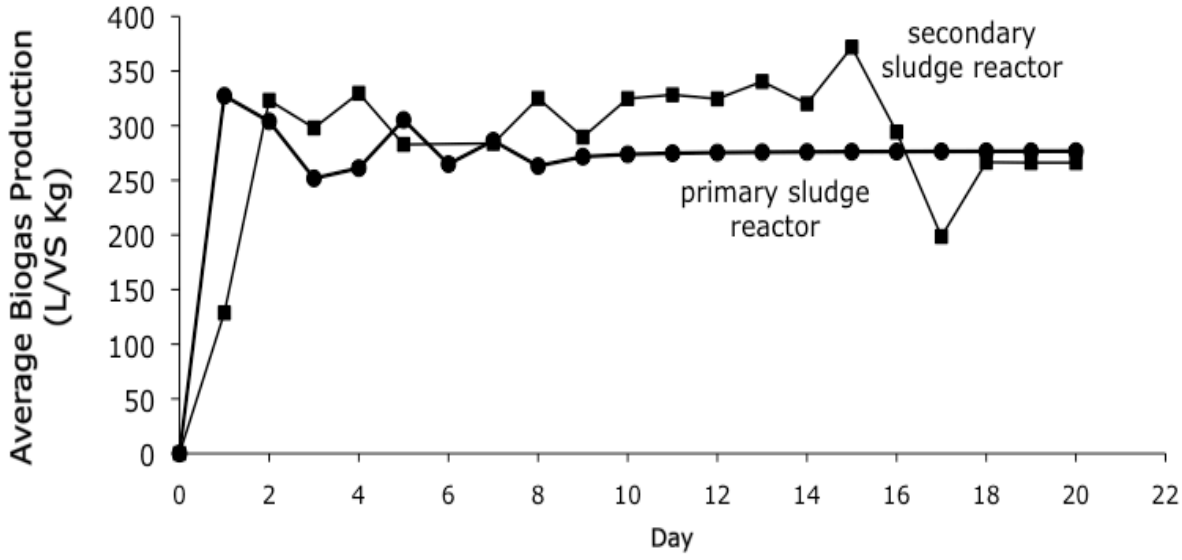

Figure 3-4 Average biogas production per VS (L/VS Kg/Day) of primary (●) and secondary sludge (■) in semi-continuous feeding system.

3.2.2 VS destruction %

The VS concentration represents the biodegradable organic fraction in the sludge. The VS destruction calculated by Van Kleeck equation (see **Section 2.4.1.2** for details) is only valid in system where the volume of sludge does not change during the digestion, which is the case in this experiment. This equation does not consider the solid loss in the inoculum, and thus may underestimate the actual VS destruction. Primary sludge contained 40% more organic substrates as compared to secondary sludge. According to Van Kleeck equation for VS destruction, primary sludge has achieved 72% of VS destruction, while secondary sludge only has 57% organic content digested (Table 3-3).

Table 3-3 VS destruction (%) of primary and secondary sludge reactor during the 20 days HRT

VS destruction (%)	
Primary Reactor	72.09
Secondary Reactor	57.58

3.2.3 pH and VFA

The pH value of the bulk liquid within the reactor indicates acid accumulation within or loss of alkalinity from the digester; both reactors in this study have shown stable pH during the 20 days HRT (Figure 3-5). The Primary sludge reactor has a slightly lower pH (average 6.8) compared to secondary sludge reactor (average 7.2), as the organic acids (primarily acetate) were produced more readily in the primary sludge reactor compared to that treating secondary sludge due to its higher bio-degradation rate.

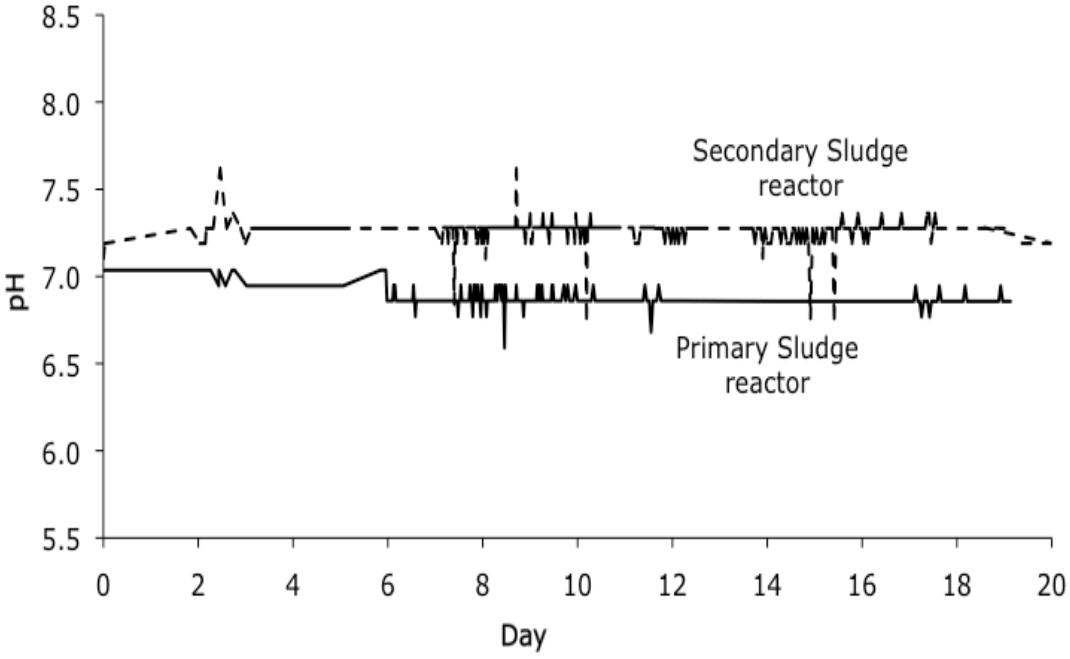

Figure 3-5 pH of primary sludge and secondary sludge reactors in semi-continuous feeding system.

Volatile fatty acid (VFA) is the end products of hydrolysis and food source for methanogens to produce methane gas in anaerobic digestion. Accumulation of VFA brings down the pH and inhibits methanogenic activity. The optimum pH for the sensitive methanogens ranges from 6.5 to 8.2 (Buyukkamaci and Filibeli 2004; Appels et al. 2008). High VFA concentration in the effluent of a digester indicates signs of overloading which can lead to digester failure. In this experiment, the VFA

concentration in the primary sludge reactor was never found higher than 10 mM, with no accumulation of propionic or butyric acids was observed in the digester (Figure 3-6a). The pH level of the primary sludge reactor remained within the stable range, suggesting the reactor was performing steadily during the 20 days experiment. Accumulation of VFA in the secondary sludge reactor was found the be insignificant (less than 5 mM), and the pH remained above pH 7 throughout the experimental period (Figure 3-6b). Note that the primary sludge reactor had a higher VFA concentration compared to the secondary sludge reactor which supports the hypothesis that the hydrolysis rate is higher in the primary sludge reactor than that of the secondary sludge reactor.

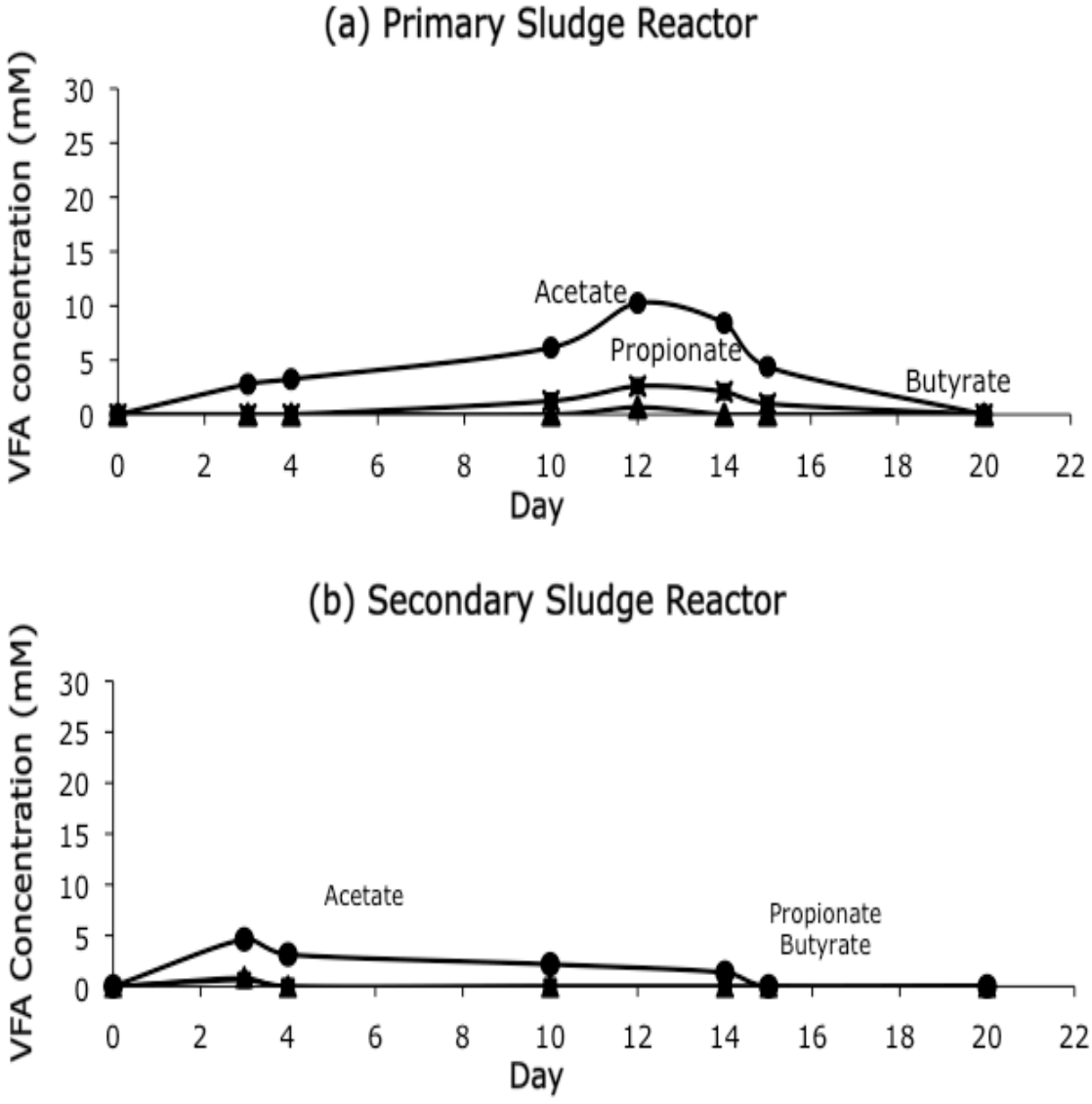

Figure 3-6 VFA concentration (mM) of the effluent from (a) primary sludge and (b) secondary sludge reactor in semi-continuous feeding digester.

3.2.4 Conclusion

Results from both batch and semi continuous anaerobic digestions are inline with literatures (Gavala et al. 2003), indicating that VS in primary sludge from Woodman Point WWTP is readily biodegradable (> 90% VS destruction) while only 60% of VS in secondary sludge can be readily digested. It seems sensible to treat the two sludges differently.

For primary sludge, with its higher biogas production and VS destruction, the feeding rate or HRT can be reduced so that the energy cost of anaerobic digestion can also be decreased. Secondary sludge, on the other hand, was most likely to be limited by its hydrolysis rate. Pre-treatment prior to anaerobic digestion should increase its bio-degradability.

In the next series of experiments, primary sludge reactor was operated at 16-day HRT to examine if primary sludge could withstand higher feeding rate whereas secondary sludge was treated with several pre-treatment methods to investigate which method could effectively improve the digestibility of secondary sludge.

3.3 Semi-continuous (fill and draw) anaerobic digestion of primary at reduced HRT

3.3.1 Reducing HRT from 20 days to 16 days

3.3.1.1 Biogas production and VS destruction

The high degradation rate observed for primary sludge in anaerobic digestion can be used as an advantage for anaerobic digestion by enabling a faster digestion and hence a reduction in HRT, by increasing the feeding rate. However, increasing the feeding rate may cause other problems such as the washout of slow growing bacteria (Mara and Horan 2003) and therefore accumulation of VFA. In this experiment, the HRT of the reactor was reduced to 16 days, with the feed rate increased from 40mL to 50mL per day.

Results shows that during 16-day HRT operation, the biogas production from the primary sludge reactor started to decrease on day 3 and dropped continuously to less than 50% of its original rate within 12 days (Figure 3-7). Noted that the methane content of the biogas also dropped over this time (from 55% to 41%) (Figure 3-7). It was expected that an increase in loading rate would provide an increase in biogas production as reported by Carnaje (1995) who found a 10-30% increase in loading rate resulted in a proportional increase in the gas production rate. This increase in biogas production, however, was not observed in the current experiment.

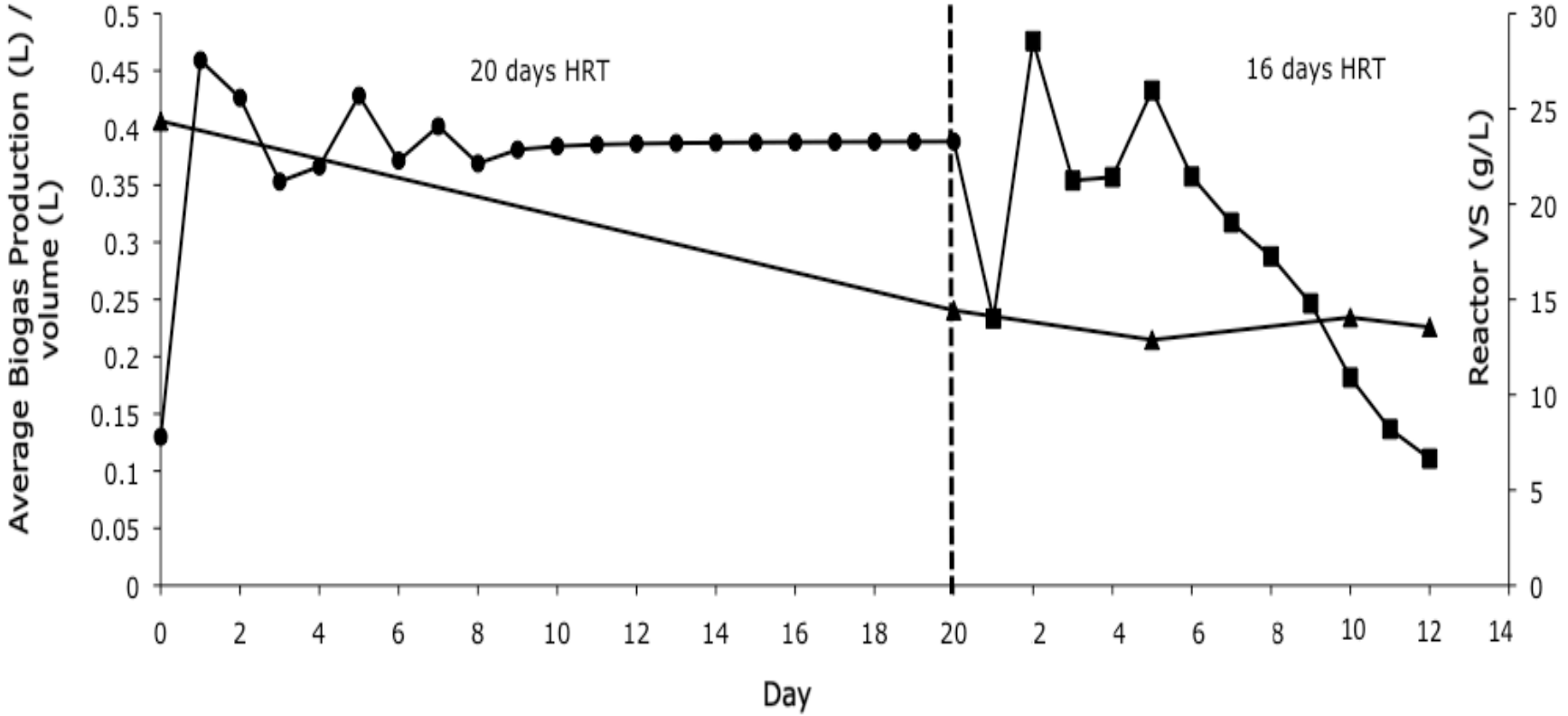

Figure 3-7 Biogas production (L/L/day) and VS (▲)(g/L) of primary sludge reactor from 20 days (●) to 16 days (■) HRT. The biogas production of 20 days HRT is stable but the biogas production started to decrease after day 3 of a higher loading rate (16 days HRT). Feeding was stopped at day 12 due to high acidity and VFA accumulation in the reactor. The VS of the reactor was reduced by around 50% from the commencement of the higher loading rate (from 24 g/L to 13.5 g/L).

VS destruction remained almost constant during 12 days operation indicating that hydrolysis continued at the same level (Figure 3-8). This reconfirm that hydrolysis in the primary sludge reactor was not the limiting step. In this case, it is expected that the hydrolysed substrates would have been converted into organic acids (VFAs) and accumulated in the system. Consequently, the VFAs concentration was measured.

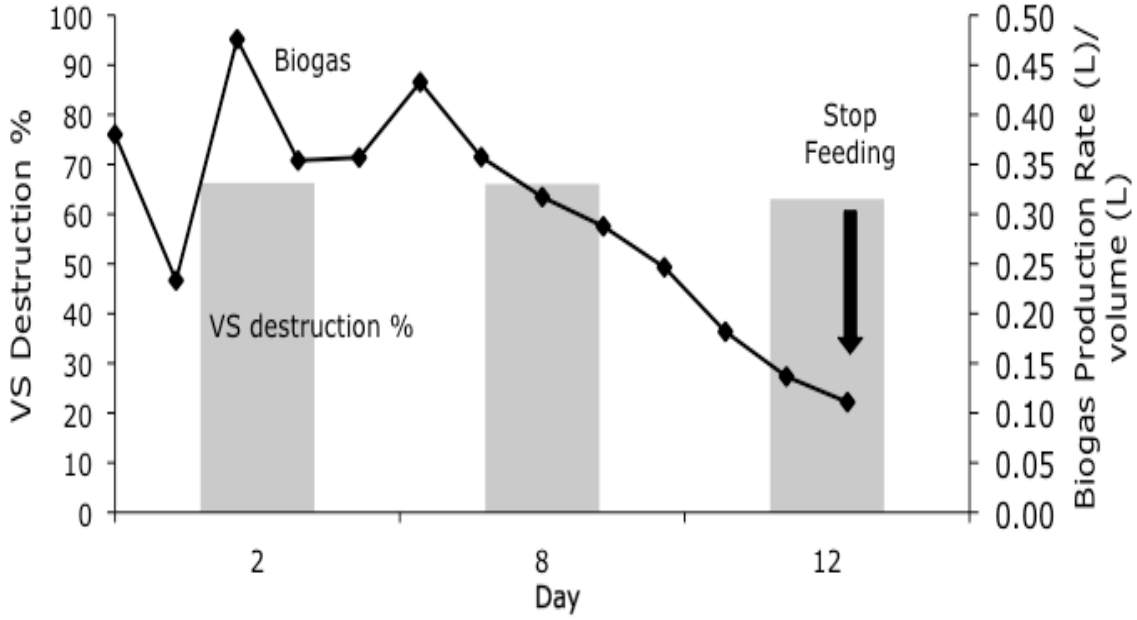

Figure 3-8 VS destruction % (column) and biogas production rate (◆) (L/L/day) during 16 days HRT. The VS destruction % of the reactor on day 12 is not much different from that of day 1.

3.3.1.2 pH and VFA inhibition

VFA concentrations were measured before every feed, and the results showed in Figure 3-10 that there were VFA left over before each subsequent feeding, and this eventually led to high concentration of VFA. The pH of the reactor shown in Figure 3-9 was still within the optimum pH value for methanogens ranges of 6.5 to 8. This is possible due to high buffer capacity of the reactor. Studies (Pullammanappallil et al. 2001; Ahring et al. 1995) indicated that digester failure caused by VFA toxicity is not significant when concentration is below 50mM. In fact, the methane production was

found to increase with the concentration of VFA up to 50mM (Ahring et al. 1995). However, results from this study found otherwise.

It should be point out that at shorter HRT, more substrate was provided and, at the same time, more biomass was removed from the digester. The slow growing methanogens are more likely to be affected compared to the fast growing acetogens. The washout of methanogens could explain why methane production was significantly low at VFAs concentrations below 50mM.

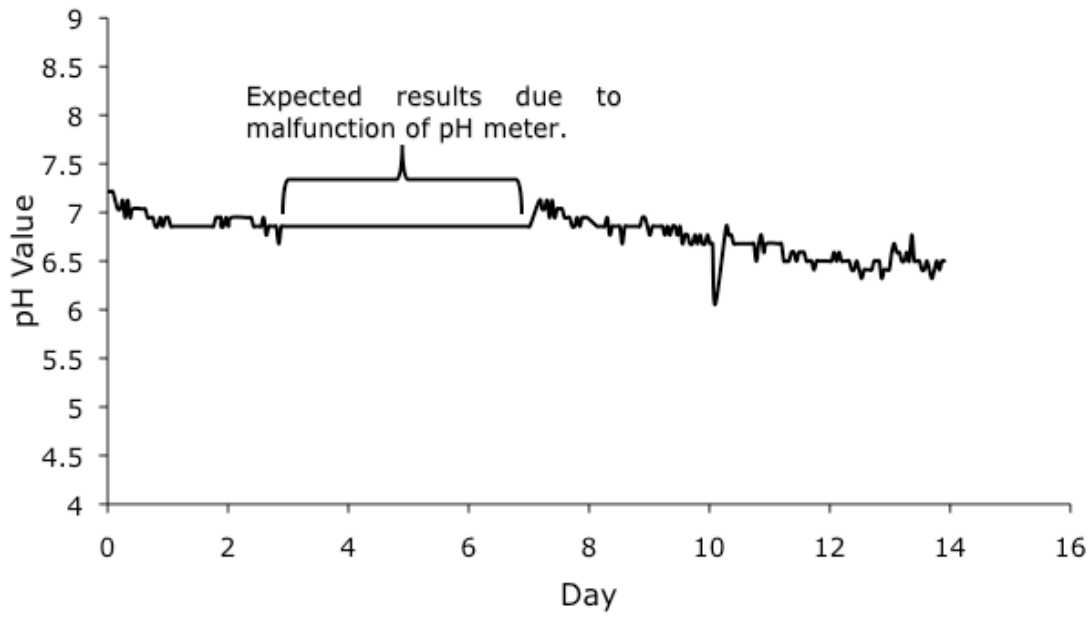

Figure 3-9 pH level of primary sldge reactor in 16 days HRT. The pH level reduced from 7.2 to 6.5.

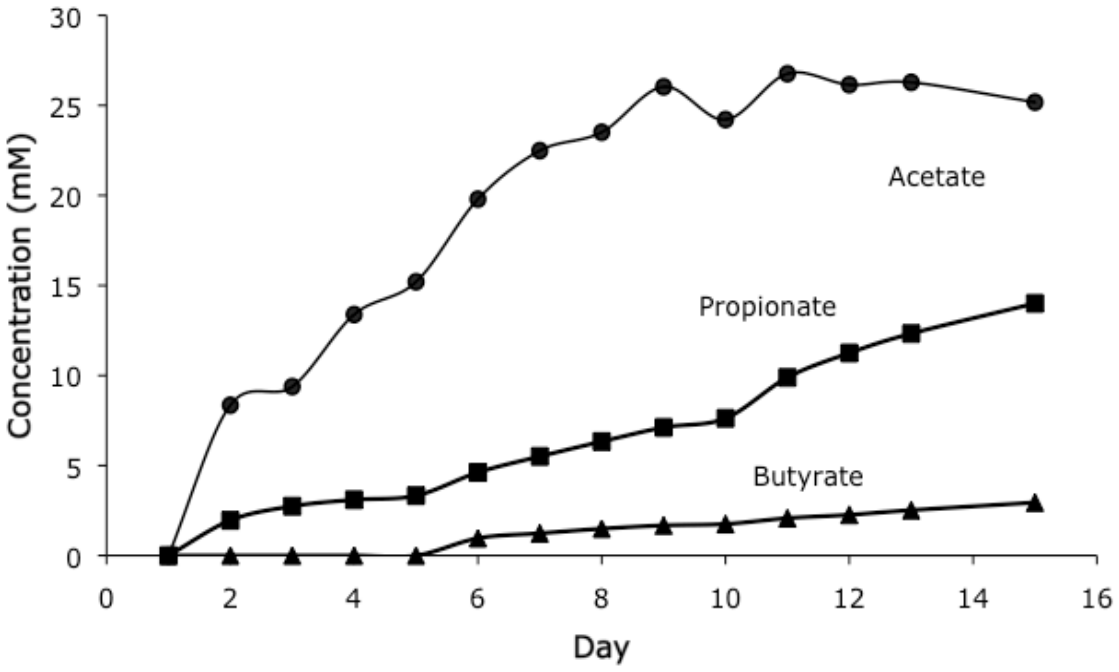

Figure 3-10 VFAs (Acetate ●, Propionate ■, Butyrate ▲) concentration of primary sludge reactor during 16 days HRT. Acetate concentration is the highest among the three VFAs, reaching around 26 mM when the feeding is stopped (Day 12). The concentration of VFAs did not reduce even when feeding is stopped (after day 12).

3.3.1.3 Hydrogen partial pressure inhibition due to shock loading

In a stable anaerobic digestion process, the reduction of pH caused by VFA and hydrogen is usually neutralized the alkalines produced by methanogens in the form of bicarbonate and ammonia (Appels et al. 2008; Pullammanappallil et al. 2001). Hydrogen and acetate are the main food source for methanogens to produce methane gas. Nevertheless, at high concentration of dissolved hydrogen, the conversion of long chain VFA to acetate is inhibited. As proton (H^+) ions increased in the anaerobic digester, it affects the chemistry pathway of certain substrates degradation. At high concentration of dissolved hydrogen, the activity of obligate hydrogen-producing acetogens (OHPA), which converts propionate and butyrate into acetate, hydrogen and carbon dioxide, is inhibited (Mara and Horan 2003). Partial pressure of hydrogen needs to be below 10 Pa in order to maintain the syntrophic relationship between

OHPA and hydrogen utilizing methanogens in anaerobic digestion (Mara and Horan 2003).

In this experiment, the feeding was done in the form of shock loading (once per day). The high substrate availability might have caused high partial pressure of hydrogen in the system within a short time after feeding, due to rapid hydrolysis. Figure 3-11 shows hydrogen partial pressures of day 12 after the feed. Two hours after the feed, the partial pressure of hydrogen in the reactor increased sharply to around 7.8 Pa. At this level of partial pressure, propionate or butyrate degradation could be inhibited. (Cord-Ruwisch et al. 1997) reported that partial pressure of hydrogen around 7-8 Pa in a semi-continuous loading system represents a warning signal of digester overloading. The hydrogen partial pressures of previous feeding days were not measured due to unavailability of the instrument.

Although the partial pressure was then reduced to 4 Pa after 6 hours, the biogas production was not recovered, and there was no decrease in the VFA concentration observed in the system (Figure 3-10**;** Figure 3-11). No decrease of VFAs concentration was observed until one week after day 12 (stop feeding), suggesting that once inhibition of anaerobic digester occurred, the recovery of digester reactivity is difficult. This result implies that the daily feeding regime used in this experiment may contribute to the failure of the reactor. If the feed was added into the reactor gradually, the high hydrogen partial pressure could be prevented, and the VFA can be formed gradually and accumulation of VFAs can be avoided.

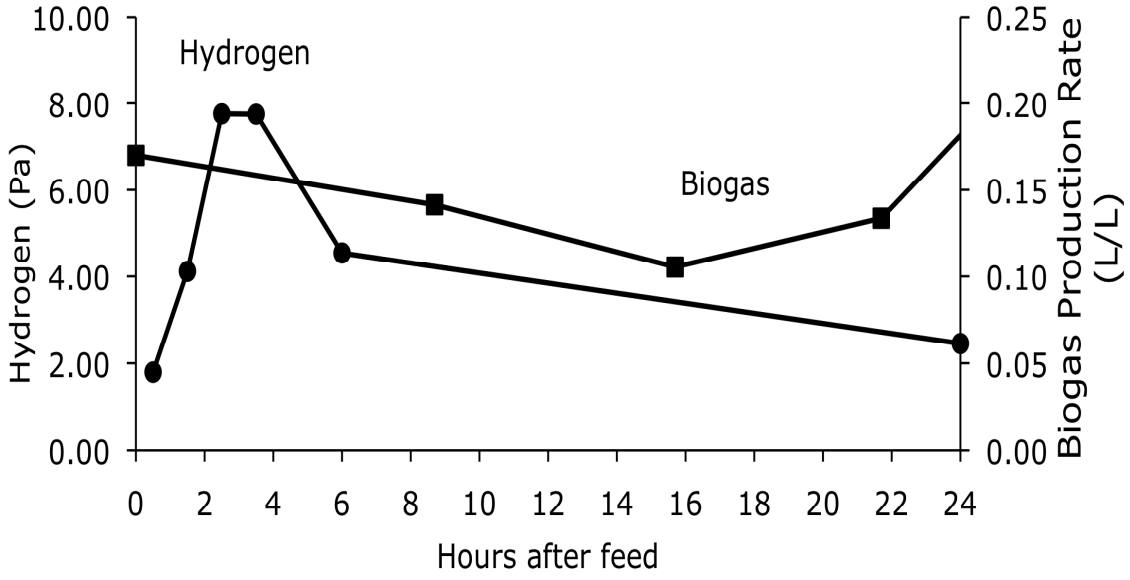

Figure 3-11 Hydrogen (●) partial pressure (Pascal) and biogas (■) production rate (L/L/day) of primary sludge reactor after feeding on day 12 (digester fail).

3.3.1.4 Mixing effect on anaerobic digester performance

In this experiment, the stirring speed of the primary sludge reactor was set at 600 RPM to ensure full mixing of organic feed in the reactor. The stirring speed might have caused the low performance of the primary sludge reactor. In (Hoffmann et al. 2008), reactors with high mixing (500 RPM, 1500 RPM) were found to have high VFA concentration and low biogas production. However, the negative impact of intense mixing on biogas production was only found during the startup stage in anaerobic digestion but not during steady-state periods (Hoffmann et al. 2008).

It was explained that, high mixing intensities in anaerobic digester will disrupt the synthrophic relationship between VFA consuming bacteria and hydrogen-utilizing methanogens and reduces methanogenic centers which are important for complete conversion of the inflow of VFAs (McMahon et al. 2001; V.A. Vavilin and Angelidaki 2005). It was suggested by (V.A. Vavilin and Angelidaki 2005), vigorous mixing is not suitable for methanogenesis limiting system as it suppress the methanogenic centers from growing. In this experiment, the pH (Figure 3-9) and VFA

profiles (Figure 3-10) has shown that primary sludge reactor was methanogenesis limiting during 16 day HRT.

It is possible that the mixing intensity of the reactor has some negative impact on the digester performance, but it is not clearly shown in this experiment as the same mixing was used in 20 days HRT. Therefore, it is hard to just conclude if the mixing of primary sludge has affects the VFA degradation and methane production in this experiment, as further investigations are still needed.

3.3.1.5 Conclusion

According to the results above, operation of the primary sludge reactor at 16-day HRT has suffered from overloading, and failed. The failure of the digester is believed to cause by a combination of several reasons, including bacteria washout, mixing and shock loading. In order to reduce the HRT of primary sludge reactor, the problems discussed above need to be addressed.

3.4 Does biomass recycling assists primary sludge reactor at shorter HRT?

The previous experiment showed that the primary sludge reactor was overloaded in 16 days HRT possibly due to the washout of slow growing methanogens. To retain the number of methanogens in the reactor, the solid retention time (SRT) of the anaerobic digester must be larger than the HRT. Mixing intensity of the reactor was also discussed in the previous experiment, where high stirring speed might have affected the degradation of VFA negatively (Stroot et al. 2001; Kaparaju et al. 2008; Hoffmann et al. 2008).

In this experiment, the biomass was retained in the reactor by settling the effluent and recycle the solids back into the reactor. (Sulaiman et al. 2009) demonstrated the effectiveness of sludge recycling on anaerobic digestion of palm oil mill effluent, where the methane production increased and COD removal efficiency increased as the sludge-recycling rate increased. As the settled solids were returned back into the

reactor, minimal loss of microoganisms (methanogens) is assumed and hence the methanogenesis rate can be improved.

To address the possible negative effect of the shear force on VFA degradation caused by high speed stirring, the stirring speed of the reactor was lower (200 RPM) than the previous experiment (600 RPM).

3.4.1.1 Operation procedure

The inoculum of the reactor was changed with new digested sludge collected from Woodman Point WWTP. The reactor operation methods are described in **Section 2**, except the stirring speed was turned down to 200 RPM in this experiment.

The recycling rate of sludge back to the reactor is 14mL/day. Effluent of reactor was centrifuged at rotation of 4600 RPM for 25 mins. The settled solids were then mixed with 50mL of primary sludge feed and put into the reactor.

3.4.1.2 Biogas Production

The biogas production of primary sludge reactor operated at 16-day HRT with sludge recycle increased from day 1 to 3 and continued to maintain within 0.84 – 1.1 L/L/day for the rest of 16 days operation, and the methane composition was around 66 – 69% of the total biogas produced (Figure 3-12). The biogas production in the first three days was lower (< 0.8 L/L/day) suggested that the reactor was still adapting to the new feed. The biogas production showed that through biomass recycling, the primary sludge reactor is able to produce biogas steadily for 16 days HRT as opposed to the previous experiment (see **Section 3.3.1**). As the biogas production in this experiment is much higher than the biogas production in **Section 3.1**, this indicated a possible of gas leakage in that experiment.

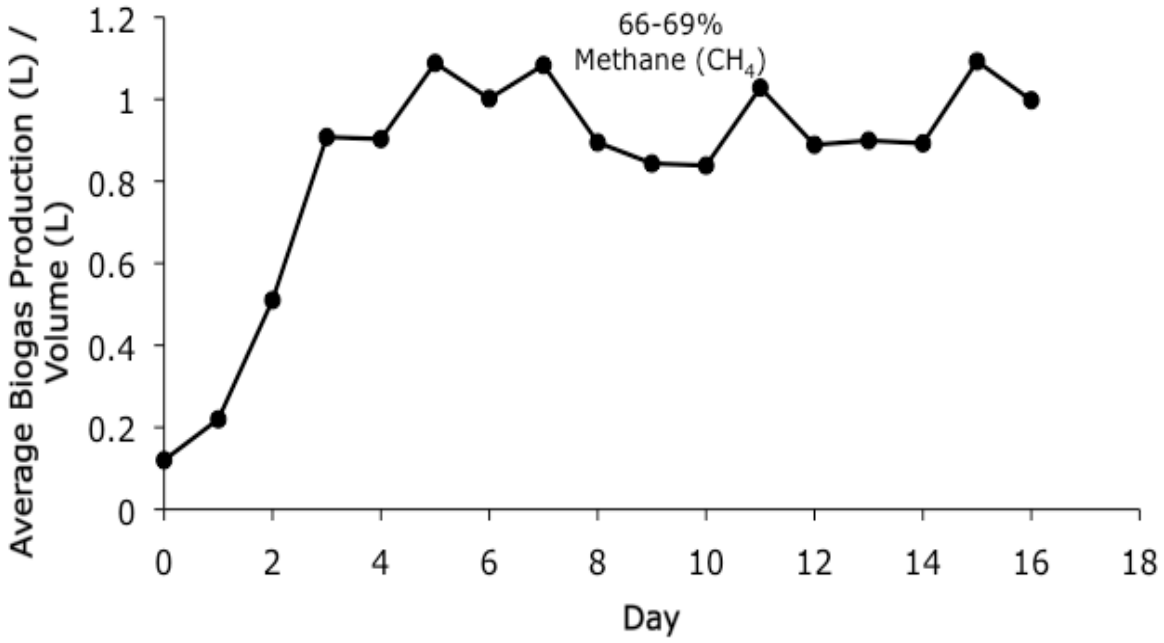

Figure 3-12 Biogas production (L/L/day) of primary sludge reactor in biomass recycling system at 16 days HRT. Methane gas is about 66 – 69% of total biogas.

As 100% of the solids from the effluent were recycled back into the reactor, the bacteria, in particularly methanogens, should have been retained in the reactor. In this case, the SRT of the reactor was longer than its HRT, as the solids were put back into the reactor every time. Hence, the solid concentration (i.e. biomass) in the reactor should have increased, and improve the processing capacity of methanogens in the reactor. The stable biogas production in this experiment showed that retaining the slow growing methanogens is an important factor for anaerobic digester to work under short HRT.

3.4.1.3 pH and VFA profile

From the previous experiment, the pH value dropped to 6.5 and the VFAs accumulated during 16 days HRT (Figure 3-9**;** Figure 3-10), causing the reactor to fail. In this experiment, the pH and VFA in primary sludge reactor in this experiment were found to be stable during the operation (Figure 3-13**;** Figure 3-14). The pH value of the reactor stayed above pH 7 all the time, although a slight decrease was observed in the first two days (Figure 3-13).

The VFAs concentrations of primary sludge reactor before each feeding are shown in Figure 3-14. There are some residual VFAs in the beginning of the 16 days operation. As the number of days increased (number of recycles increased), VFAs concentrations decreased. This was believed to be the result of the VFA-utilizing methanogens increasing in the system. (Figure 3-14).

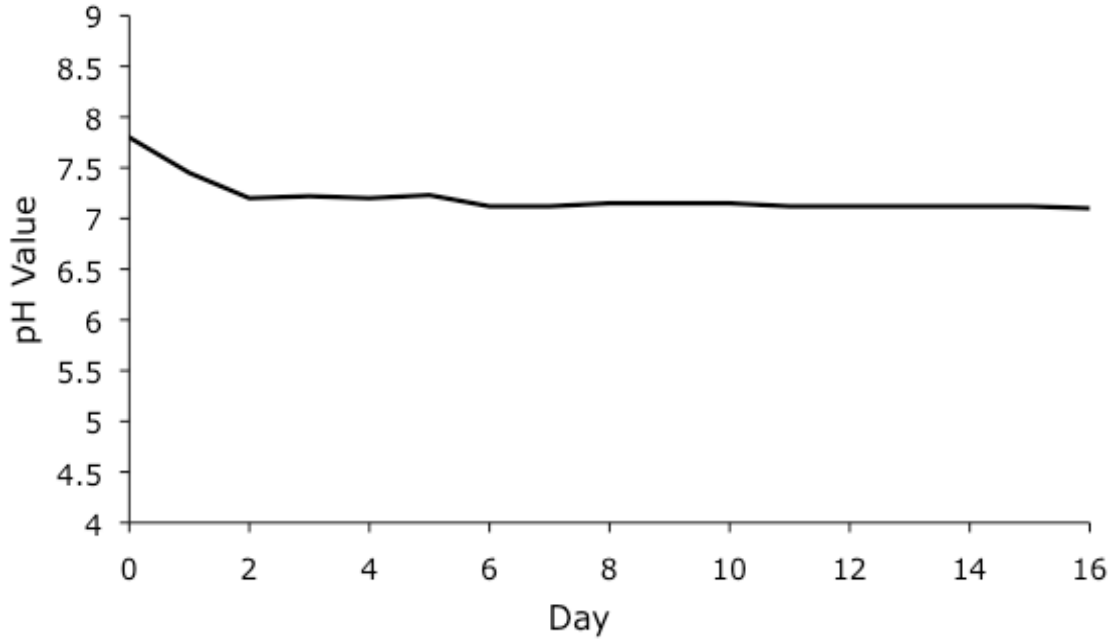

Figure 3-13 pH value of primary sludge reactor at 16 days HRT under biomass recycling system. The pH of the reactor maintains at desirable level (> 7.1) all the time.

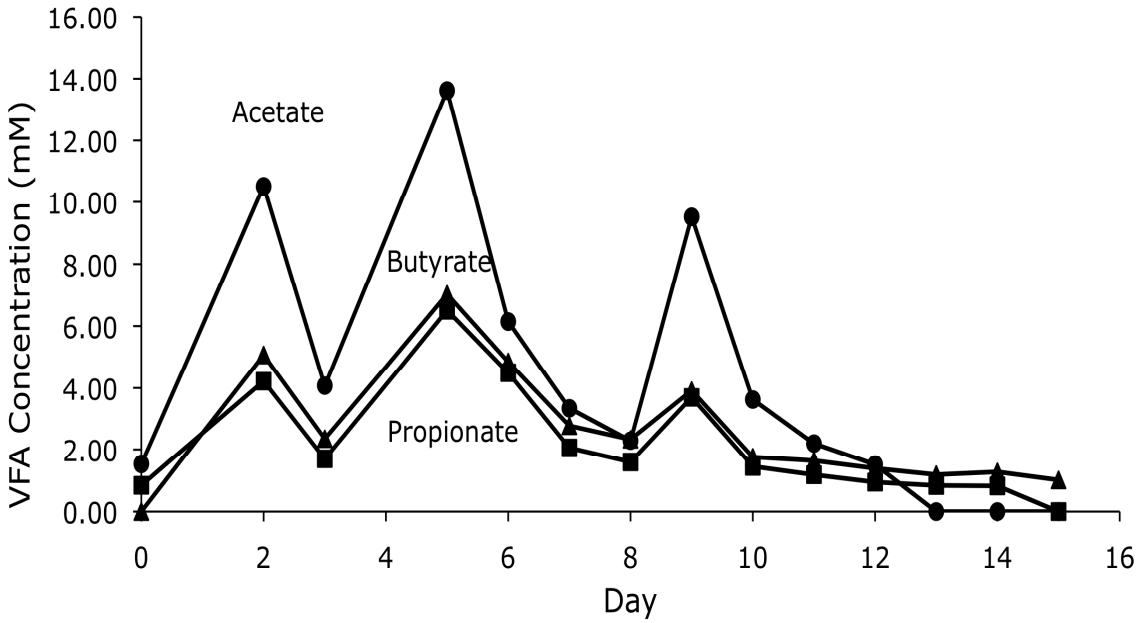

Figure 3-14 VFA (Acetate ●, Propionate ■, Butyrate ▲) concentration in primary sludge reactor under biomass recycling operation.

The overall performance of primary sludge reactor under biomass recycling system showed that as the SRT of the system increased, the reactor could work steadily at shorter HRT. The biogas production of primary sludge at 8 days HRT under biomass recycling system was found to have increased to 1.3-1.4 L/L/day in the first two days and no VFA accumulation was observed (Results not shown). However, due to time limitation, the experiment was not completed. Therefore, further investigations are required to confirm if biomass recycling system can work properly at HRT lower than 10 days.

As the number of methanogens in the system increased, the working capacity of primary sludge reactor was improved. There is no costly infrastructure needed if the recycling system is to be implemented in real scale WWTP. In WWTP, there are usually centrifuges built for biosolid dewatering. Furthermore, by recycling back the sludge into the reactor, the volume of sludge could be reduced, and cost for disposal could be reduced as well. However, in this experiment, the solids were returned 100% into the reactor, this may not possible for the full-scale anaerobic digesters. Further research is required to find out the suitable recycle rate of sludge to be returned back into the reactor.

3.5 Pre-treatments for secondary sludge in anaerobic digestion

3.5.1 Introduction

Secondary sludge is the excess biomass in secondary treatment systems. Most of the organic content of secondary sludge is stored within the microbial cells. However, microbial cells are hard to degrade as the cell membrane serves as a protective cover for the cells to resist osmotic lysis (Weemaes and Verstraete 1998). Secondary sludge contains a mixed community of microbial groups. Some of them are facultative bacteria, which could still survive in an anaerobic digester. These slow down the hydrolysis in anaerobic digestion of secondary sludge, and hence require a longer hydraulic retention time (Appels et al. 2008).

Hydrolysis limitation in anaerobic digestion of secondary sludge was shown in **Section 3.1**, where the reactor fed with secondary sludge produced less methane than the reactor fed with primary sludge. In the batch anaerobic digestion, only 46% of secondary sludge VS were converted to biogas. Similar findings were found in the semi-continuous feeding reactor operated at 20 days HRT (***Section 3.2)***, where the biogas production of the secondary sludge reactor was found to be low and VFA (hydrolyzed product) concentrations were always low in the system.

In order to increase the efficiency of anaerobic digestion for secondary sludge, the rate of hydrolysis needs to be improved. Applying pre-treatments prior to anaerobic digestion is one of the options for secondary sludge to increase its degradability. This has been shown in many studies, where the anaerobic digestion of secondary sludge was improved through various pre-treatments. The main purposes of most pre-treatments are to cause cell dispersion, reduce sludge volume, increased pathogen inactivation and reduce odors and increase methane production (Angelidaki and Sanders 2004; Weemaes and Verstraete 1998; Wilson and Novak 2009; Appels et al. 2008).

There are many different pre-treatments that are available for anaerobic digestion of secondary sludge, such as thermal, chemical (alkaline, acid), enzymes, ultrasound, high pressurized homogenizers, etc. (Weemaes and Verstraete 1998; Appels et al. 2008; Valo et al. 2004; Chu et al. 2001; Pilli et al. n.d.).

In the following experiments, two pre-treatment methods have been compared in terms of methane production, VS destruction, and energy consumption. Besides high methane production, the energy gained from pre-treated anaerobic digestion needs to be significantly higher than the energy consumption to support the feasibility of the pre-treatments. Most of the studies only show the improvements in methane production induced by pre-treatments, but the energy usage of the pre-treatments are rarely discussed (Yang, X. Wang, and L. Wang 2009).

In the following experiment, two pre-treatment methods were compared in which pre-treatment is the most efficient method to improve anaerobic digestion of secondary sludge. The two pre-treatments studied in this experiment were thermal and electrolysis, details of experimental procedures were described in **Section 2**.

3.5.2 Thermal pre-treatment

Heat treatment generally breaks down the chemical bonds of cell wall and membrane in the sludge, and causes cell lysis to occur which can favor the release of organic components (Valo, Carrere, and Delgenes 2004; Gavala et al. 2003). There are many studies that have investigated the effectiveness of thermal pre-treatment for improving the hydrolysis of secondary sludge in anaerobic digestion (Wilson and Novak 2009; Gavala et al. 2003; Valo, Carrere, and Delgenes 2004; Yang, X. Wang, and L. Wang 2009).

In this experiment, thermal pre-treatment had been conducted on secondary sludge prior to anaerobic digestion to examine the effectiveness of thermal pre-treatment on sludge degradation and methane production. From literature, many studies have shown a wide range of effective temperature for thermal pre-treatment, and the results vary due to the different sludge feed used in the studies (Tanaka et al. 1997; Weemaes and Verstraete 1998; Wilson and Novak 2009; Appels et al. 2008).

In order to examine the effect of thermal pre-treatment, the secondary sludge in this experiment was pre-treated at 80°C, 100°C, 120°C and 150°C for 1 hour. The effectiveness of thermal pre-treatment would be evaluated based on their VS and

COD solubilisation and the methane production from anaerobic digestion of pre-treated sludge.

3.5.2.1 Volatile solid destruction and COD solubilisation

Volatile suspended solids (VSS) concentration and soluble chemical oxygen demand (SCOD) concentration are usually used to represent the organic component in the substrate. VSS and SCOD define the transfer of particulate organic matter (VSS) to soluble organic (SCOD) after thermal pre-treatment (Mottet et al. 2009).
The calculation is based on the following equation:

$$\mathbf{S_x\ (\%) = (S_t - S_u) / VS * 100}$$ (Mottet et al. 2009)

Where S_x is the solubilisation of COD or VS; S_t and S_u are the soluble fraction (SCOD, soluble VS) in treated and untreated sludge, respectively; VS is the particulate fraction of untreated sludge.

Results in Table 3-4 showed that thermal pre-treatment increased the soluble fraction of organic in the sludge. In Table 3-4, the VSS values of treated secondary sludge decreased with increasing temperature. The VS solubilisation increased as VSS decreased. At 150°C, 32.85% of VS were converted into soluble form and at 80°C only 15% were converted (Table 3-4). This shows that at higher temperature, more particulate matter were degraded and converted into soluble organic compounds. To be noted, the VS solubilisation of 100°C treated sludge is higher than that of 120°C (Table 3-4). This does not match with the observation found in SCOD, where 120°C treatment induced higher SCOD than 100°C (Table 3-4). Hence, this outlier could be due to technical mistakes.

The COD solubilisation of treated sludge also showed similar trend as VS solubilisation. The increased temperature results in increased soluble COD in the sludge (Table 3-4). These findings are similar to studies done by (Mottet et al. 2009; Wilson and Novak 2009). To be noted that, little difference was found between the solubilisation of COD of 80°C and 100°C, and when the temperature was at 120°C, a huge increment (from 7.48% to 19.70%) was observed in the solubilisation of COD (Table 3-4).

Table 3-4 VSS, VS solubilisation (%), SCOD and COD solubilisation (%) of secondary sludge treated at different temperature.

Temperatures (°C)	*VSS (g/L)*	*Solubilisation of VS (%)*	*SCOD (mg/L)*	*Solubilisation of COD (%)*
80	12.70	14.99	3594.68	7.33
100	11.62	21.74	3632.25	7.48
120	12.06	18.99	6725.93	19.70
150	9.84	32.85	8266.50	25.79
Untreated (Control)	15.10		1740.98	

The results of VS and SCOD solubilisation (%) showed that through thermal treatment, soluble fraction of organic content increased in secondary sludge. However, this information is not adequate to conclude which temperature is best for secondary sludge anaerobic digestion. The methane production of treated secondary sludge would be discussed in the next section.

3.5.2.2 Methane production

The methane production of secondary sludge increased as the pre-treatment temperature increased (Figure 3-15). Secondary sludge treated at 150°C produced the most methane gas (357.10 mL/VS g), which was about 58% higher than that of untreated sludge (Figure 3-15). Thermal pre-treatment at 80°C has the least effect, where the methane production was only 10% higher than that of untreated secondary sludge. In a study done by (Nielsen et al. 2010) has shown that secondary sludge pre-treated in 80°C water bath for 10 hours have no improvements when compared to untreated secondary sludge. Another study done by (Skiadas et al. 2005), 37% more methane gas was produced compared to untreated secondary sludge when was pre-treated at 70°C for 2 days. This suggests that pre-treatment at lower temperature may requires longer duration of treatment time to improve methane production significantly and the methane production may vary with different origin of the sludge (Gavala et al. 2003).

Methane production of 100°C and 120°C treated sludge was found to be similar (<10% different), that is it does not match with the big difference shown in their COD

solubilisation (Table 3-4). It should be noted that, the methane production of 120°C pre-treated sludge was lower than that of 100°C before day 14, but since then the accumulated methane production went above 100°C methane production (Figure 3-15**).** This observation suggests that there might be some mistake in the SCOD estimation of the sample, or it may be due to the formation of soluble but hardly degradable compounds at high temperature (Mottet et al. 2009).

Overall, thermal pre-treatment is effective in improving the hydrolysis and methane production of secondary sludge. Thermal pre-treatments above 100°C are more effective in increasing methane production in comparison with methane production of 80°C pre-treated secondary sludge. However, the energy consumption of high temperature treatment need to be take into consideration to decide whether thermal treatment is feasible or not. The energy consumption of thermal pre-treatment will be discussed in **Section 3.5.4.**

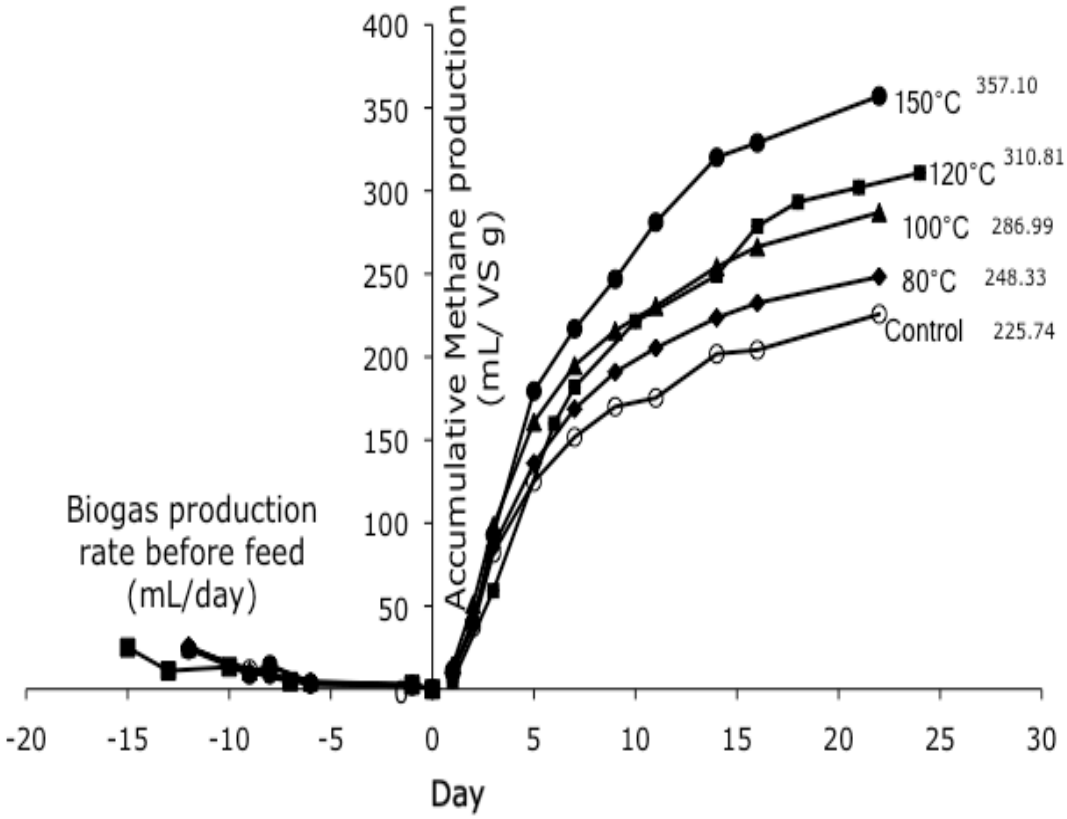

Figure 3-15 Accumulative methane production (mL) per VS (g) of thermal pre-treated secondary sludge. Feeding started from day 0. Secondary sludge pre-treated with 150°C produced the most methane gas (357.10 mL/VS g), while 80°C pre-treated secondary sludge only produced 248.33 mL/VS g.

3.5.2.3 VS destruction % after anaerobic digestion

The VS (g/L) of the remains in the serum vials were analysed after 24 days of anaerobic digestion to examine how much organic content was consumed and converted into biogas. The VS destruction % calculation is described in **Section 2.4.1.2**. The VS destruction % in overall increased with increased temperature of treatment, except at 120°C (Table 3-5). The VS destruction % of showed in Table 3-5 does not match the trend of methane production (increase with increasing temperature). The VS destruction of 120°C pre-treated sludge after anaerobic digestion is highest among all thermal pre-treated secondary sludge, 72% of the organics loss after anaerobic digestion (Table 3-5). VS destruction % of below 80°C pre-treatment is lower than that of control, and the VS destruction % reduced at

150°C pre-treatment. This suggests that even when the soluble fraction of organic content increased after thermal pre-treatment, not all solubilised organics were converted into biogas, the soluble fraction may still remain hardly biodegradable. However, the results in this experiment are not able to confirm the last point. As the aim of this experiment is to investigate the effect of thermal pre-treatment on methane production, the VFA concentration and SCOD in the serum vial during anaerobic digestion were not examined.

Table 3-5 VS destruction % of thermal treated secondary sludge after anaerobic digestion.

VS (g) in serum vial	*Before AD (VS g)*	*After AD (VS g)*	*VS destruction%*
80°C	0.32	0.16	50.03
100°C	0.32	0.15	53.00
120°C	0.32	0.09	72.20
150°C	0.32	0.12	64.08
Control (untreated)	0.32	0.12	63.85

3.5.3 Electrolysis

Acid and alkaline pre-treatments have been proved to be effective in enhancing the hydrolysis of secondary sludge in anaerobic digestion (Lin, C. N Chang, and S. C Chang 1997; X. Liu et al. 2008; Valo et al. 2004; Vlyssides and Karlis 2004). However, acid/alkaline pre-treatments usually achieved with adding chemicals and require neutralization after the pre-treatments with chemical as well (Appels et al. 2008). Addition of chemicals in large-scale anaerobic digestion system is not feasible as the cost for large amount of chemical is high.

In order to avoid the addition of chemicals, the electrolysis pre-treatment is proposed. This method is an adaption of water hydrolysis, where water molecules are split into hydrogen and hydroxide ions at supply of adequate voltage, forming a pH gradient across the two electrodes (cathode and anode) (Teschke 1982; Salem 2008).

In this experiment, secondary sludge was electrolysed by using graphite sticks as electrodes for anode and cathode, and supplied with voltage power of 12 V for 30 hours. Effectiveness of electrolysis for secondary sludge anaerobic digestion would also be compared with acid and alkaline treatment.

3.5.3.1 pH changes in cathode and anode chambers

During electrolysis treatment, the splitting of water molecules occurred in both chambers, and a pH difference is formed across the two chambers. The pH of cathode chamber reached 9.4 after 30 hours, and the pH of anode chamber dropped down to pH 2.2 (Figure 3-16). When combining the two sludges, pH was found to be 5. Therefore, neutralization is required for the sludge for anaerobic digestion, as the optimum pH range for methanogens is 6.5-8 (Mara and Horan 2003). The pH changed significantly in the first 24 hours, and little changes occur the last 6 hours. Both chambers formed a pH difference of around 3.2-3.6 between the initial and finished pH. This shows that the effect of electrolysis is equal at both electrodes.

The pH in cathode chamber only increased to 9.4, which is lower than the pH usually done by other studies (pH 10-12)(X. Liu et al. 2008; Valo et al. 2004). The pH change in the cathode chamber might need longer time under the given conditions, some reactions may have occurred at the same time that neutralized the hydroxides produced or it may be due to the buffer capacity of the sludge. As the pores on the ion-exhange membrane are so small, the particulates in sludge might have blocked the membranes pores, inihibiting the ions migration. Improvements of pH changes may need further investigations, as the reason is not confirmed in this experiment.

Another possible reason for the slow pH change may be due to the resistance caused by ion-exchange-membrane that slow down the ions migration. Further investigations are needed to investigate for more suitable material to separate anode and cathode chamber.

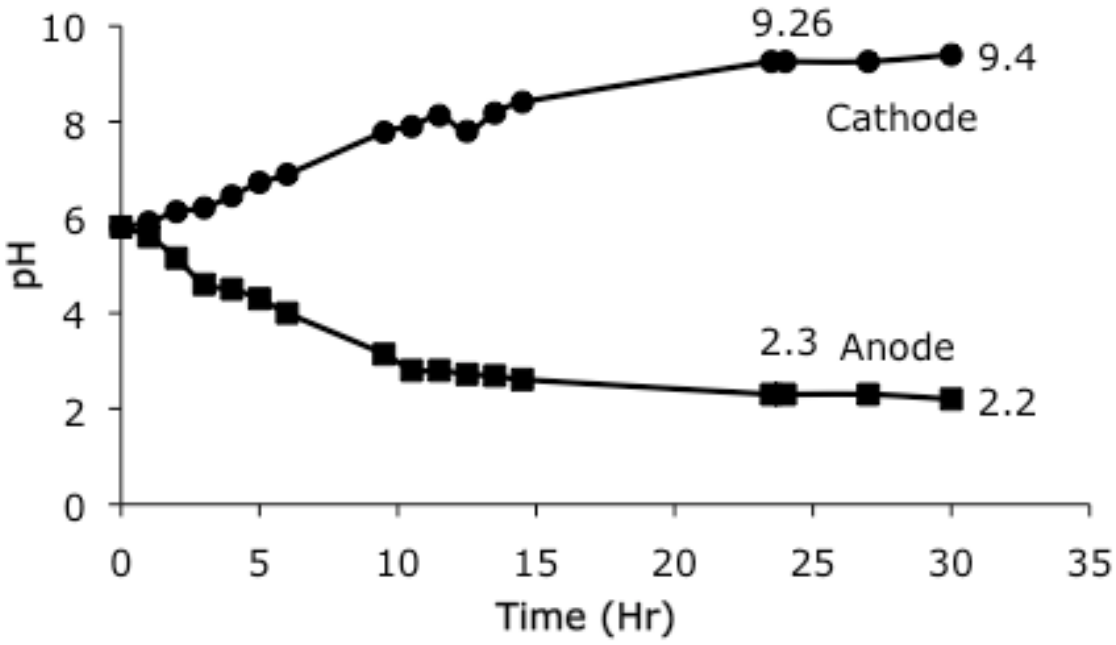

Figure 3-16 pH in each cathode and anode chamber overtime at 12 V electrolysis. The initial pH is 5.8.

3.5.3.2 VS and COD solubilisation %

The electrolysis pre-treatment and acid/alkaline pre-treatment enable the increased of soluble fraction in secondary sludge, all VSS of secondary sludge decreased after the pre-treatments (Table 3-6).

The VS solubilisation % of anode chamber is the highest among all treatments; where 32.87% of volatile solids dissolved after electrolysis. The secondary sludge treated in the cathode chamber showed slightly lower solubilisation of VS (27.37%) in comparison with that from anode chamber. In comparison with study done by (Li-jie Song et al. 2010), the VS solubilisation of secondary sludge is around 9%, the power supplied in the experiment was 5 W at a duration of 4 hours. In comparison with other studies, the VS solubilisation in this electrolysis experiment is considerably high; this may be due to the difference of operating system used, VS concentration used in each study and the origin of sludge (Gavala et al. 2003; Li-jie Song et al. 2010).

Both acidity and alkalinity pre-treatments increased the soluble fraction of organic substrate in secondary sludge at the same pH as the electrolysis chambers (pH 2.2, 9.4). In terms of VS solubilisation, acid pre-treatment (28.62%) is more effective compared to alkaline pre-treatment (26%)(Table 3-6). In a thermo-chemical study, the VS solubilisation of secondary sludge was 15% when treated with H_2SO_4 (to pH 3) and 60% when treated with NaOH (to pH 12) at 90°C (X. Liu et al. 2008). This disagree with the results found in this experiment, where the VS solubilisation of alkalinity treatment is not better compared to that of the acidity treatment, suggesting that the pH 9 may be inadequate to enhance cell disruption in secondary sludge. (Valo et al. 2004) found that the VS solubilisation % of secondary sludge increased significantly from 10% at pH 10 to 30% at pH 12. This indicates that the effectiveness of alkalinity treatment is only significant when treated above pH 10.

Table 3-6 VSS (g/L), VS solubilisation (%), SCOD (mg/L) and COD solubilisation (%) of electrolysed and chemical treated secondary sludge.

Treatments	*VSS (g/L)*	*Solubilisation of VS (%)*	*SCOD (mg/L)*	*Solubilisation of COD (%)*
Cathode	4.75	27.37	2358.45	6.09
Anode	4.31	32.87	2872.17	10.15
Acid	4.65	28.62	*results not available*	
Alkaline	4.86	26.00		
Untreated (Control)	6.94		1587.87	

3.5.3.3 Methane production

The accumulative methane production of sludge of both anode sludge and cathode sludge showed better results when compared with the untreated sludge after 22 days (Figure 3-17). The methane production of the electrolysed sludges is around 30% higher than the non-treated sludge. There is little difference found in the methane production between anode and cathode sludges, suggesting that both chambers have the equal effectiveness in improving methane production. However, the methane production of anode sludge was very low in the beginning when compared with the cathode sludge and control (non-treated) and a rapid increase occurred from day 13 to

18. This was not found in methane production of sludge treated with acid (Figure 3-18**a**). This could be due to the oxidation reaction occurred in the anode chamber during electrolysis, where organic substrates were oxidized into compounds that are harder to degrade and hence affecting the hydrolysis in the beginning (Salem 2008).
When compared the methane production of the electrolysed sludge and chemical treated sludge, both acid and alkaline treated sludge showed slightly higher (8-9%) methane production than that of the electrolysed sludge (Figure 3-18**b**). The similar methane production between electrolysed and chemical treated sludge showed that the effect of this electrolysis experiment might be mainly due to the pH changes in the sludges.

This does not agree with the finding of (Li-jie Song et al. 2010), where the electrolysis in single chamber (no pH difference in chamber) could disrupt cell membranes in secondary sludge under the condition of no pH changes occurred.

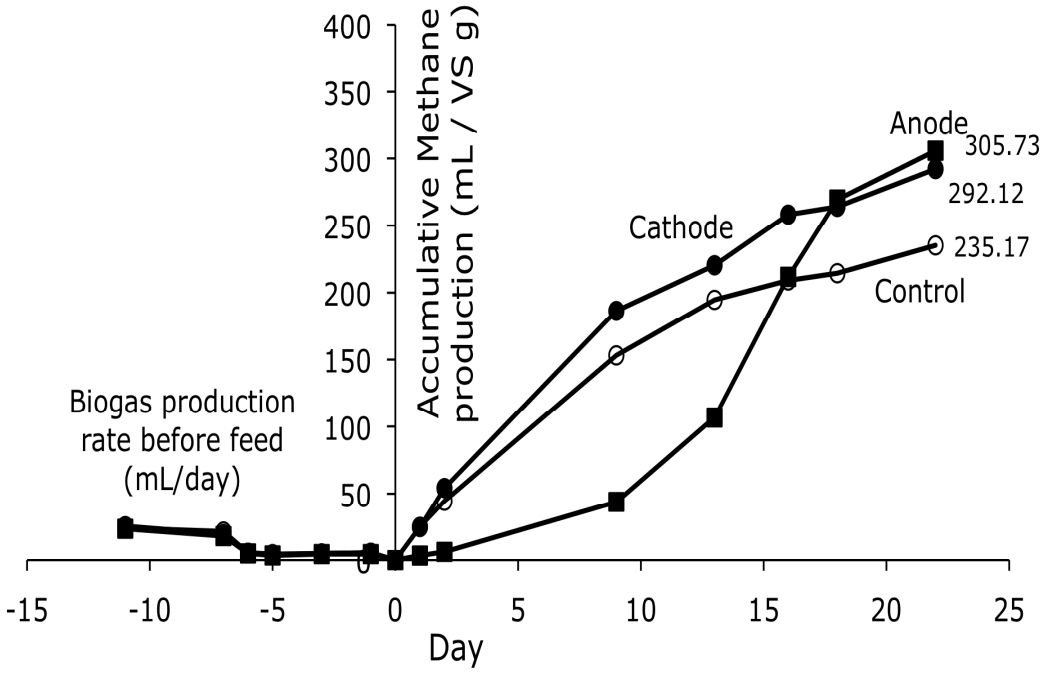

Figure 3-17 Methane production (mL) per VS (g) of electrolysed secondary sludge. Feeding started from day 0. Both sludge treated in anode and cathode produced higher methane gas compared to non-treated secondary sludge (control).

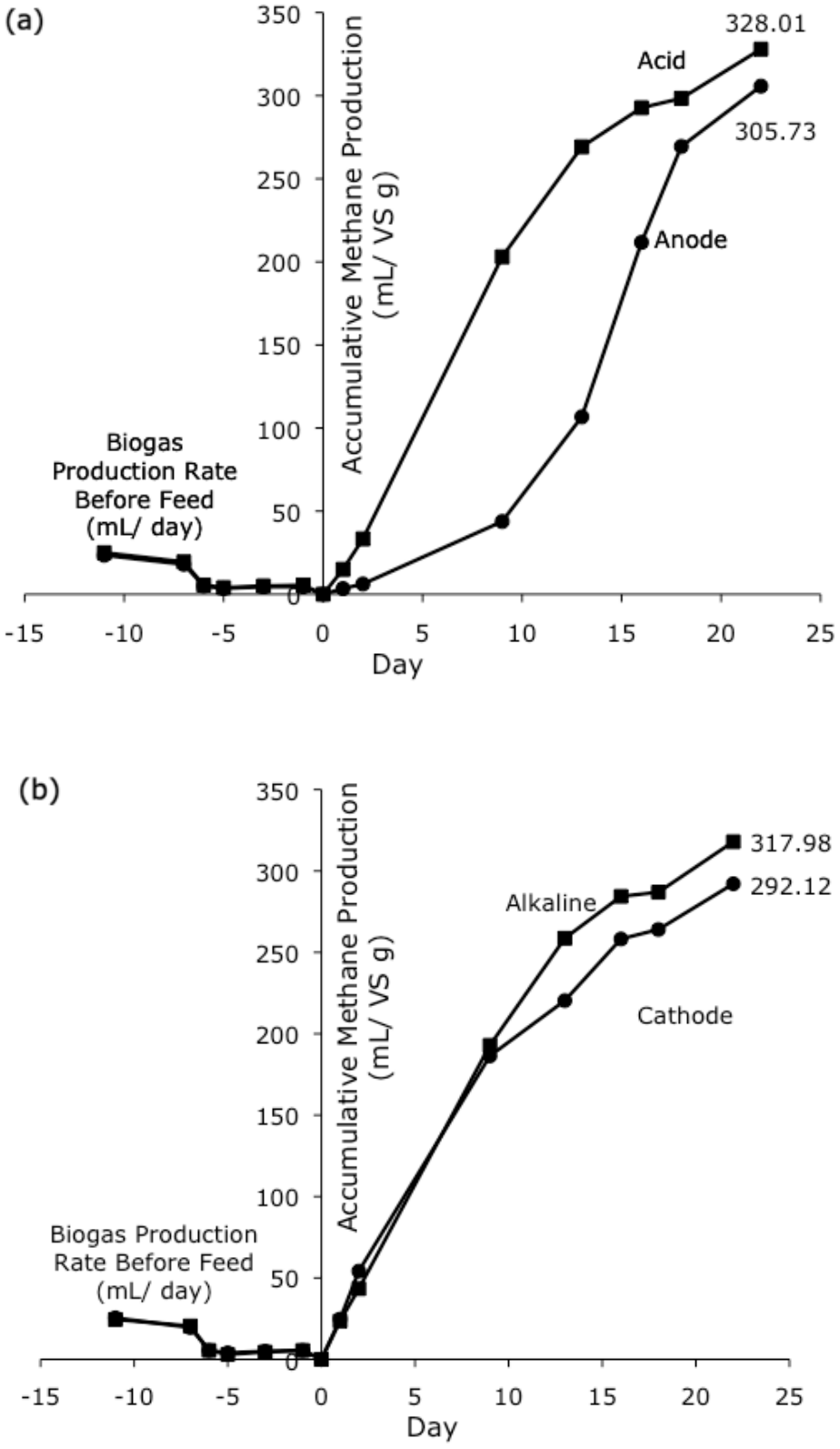

Figure 3-18 Accumulative methane production (mL/VS g) of (a) anode and acid treated sludge (b) cathode and alkaline treated sludge.

As the electrolysed sludge showed similar methane production as the chemical treated sludge, it implies that electrolysis may be a good substitute for acid/alkaline treatment, as it requires less addition of chemical reagents.

In overall, electrolysis has shown to be effective in enhancing the methane production of secondary sludge in this experiment. In this experiment, electrolysis of secondary sludge was tested at 12 V for 30 hours, no comparison results of other voltage levels or time duration were presented in this experiment. Hence, further investigations are required as this is only a preliminary study of electrolysis pre-treatment for secondary sludge.

3.5.4 Energy conversion of pre-treatments

In the previous two experiments, thermal and electrolysis pre-treatments were found to have positive effects on the methane production of secondary sludge digestion. However, the energy consumption of both pre-treatments was not discussed. The energy input of each pre-treatment and the energy gain from anaerobic digestion after pre-treatment were calculated (Table 3-7**).**

Calculation of energy is done as followed:
For example, energy input required for 80°C treatment
Assuming the volumetric heat capacity of secondary sludge is same as pure water,
Volumetric Heat Capacity, c = 4.216 J/cm^{3}K
Assume the initial temperature as room temperature = 25°C

Volume of sludge, V = 1 L = 1000 cm^3

Using the equation of thermodynamic
$\triangle$Q (thermal energy) = c* ΔT*V

= 4.216 J/cm^{3}K * (80-25) K* 1000 cm^3

= 231880 J = 231.88 kJ per liter volume

Energy output from anaerobic digestion
Volume of CH_4 produced from 1 L sludge = 3.976 L
At STP conditions, 1 L of CH_4 produces 37239 J of energy
(Chandra n.d.) (www.natgas.info, assessed 20 October 2010)

Hence, 3.976 L of CH_4 produces 147.06 kJ of energy.

Energy gain = Energy output – Energy input = 147.06 kJ/L – 231.88 kJ/L

= - 84.74 kJ/L

The energy output of thermal pre-treatment in this study was not enough to recover the energy input of the pre-treatment, as high temperature treatment requires high-energy input. The energy input for thermal pre-treatment showed in **Table 3-7** was only the energy required to raise temperature of water from room temperature to that particular temperature for treatment, it excluded the additional energy required to compensate heat loss during the thermal treatment. Therefore, the actual energy input of the thermal pre-treatment was higher than the value showed in **Table 3-7**.

In addition, water vaporization required the most energy during heating at pre-treatment above 100°C (Yang, X. Wang, and L. Wang 2009). This suggests that dewatering prior to pre-treatment may be an important factor to affect the heating efficiency of sludge. Although the energy output from this experiment was lower than the energy input of the pre-treatment, thermal treatment may be effective for parasites/pathogens removal of the sludge (Santha et al. 2006). If thermal pre-treatment were to be implemented, a more efficient heating method is required.

On the other hand, energy input of the electrolysis in this experiment was lesser than the energy output after anaerobic digestion, thus giving a positive energy gain (calculation see Appendix) **(Table 3-7)**. However, the energy gain was lower than that of non-treated sludge. The duration of the electrolysis in this experiment was very long (30 hours), if the period of treatment could be reduced, more energy could be saved. Nevertheless, as this is still a preliminary study of electrolysis pre-treatment for anaerobic digestion, further studies are required.

Table 3-7 Energy input (kJ/L) of pretreatments, energy output (kJ/L) from anaerobic digestion and net energy gain (kJ/L) of the two pre-treatments at various conditions.

Treatments		*Energy Input (kJ/L)*	*Energy Output (kJ/L)*	*Energy Gain (kJ/L)*
Thermal	80°C	231.00	148.06	-82.94
(1 hour)	100°C	316.20	171.11	-145.09
	120°C	400.52	185.31	-215.21
	150°C	527.00	212.91	-314.09
	Control	0.00	420.44	420.44
Electrolysis	Anode	48.01	182.17	134.16
(12 V for 30 hour)	Cathode	48.01	174.06	126.05
	Control	0.00	140.13	140.13

Energy input is calculated based on heat capacity of pure water.
In these experiment, 1 Litre of sludge = 16.01 g VS

4 Conclusions and Recommendations

4.1 Conclusions

On the basis of the results showed in this study, the following conclusions were drawn:

- Primary sludge and secondary sludge are very different in terms of their degradability and methane production. Primary sludge is easily degradable, while secondary sludge is hydrolysis limited. Separate approaches are required in order to enhance the methane production of the sludges.
- In attempt to increase the efficiency of primary sludge anaerobic digestion, the HRT was reduced from 20 days to 16 days. The HRT can only be reduced when the washout of methanogens was prevented, i.e. recycling biomass. The shorter HRT enable higher efficiency and also higher biogas production. The implementation of biomass recycle enable smaller size of reactor or just minor changes to any conventional anaerobic digester, i.e. requires only extra pipelines.
- Shock loading of feeding in semi-continuous feeding system caused instability of reactors, due to the rapid washout of slow growing methanogens.
- Thermal pre-treatment increased the VS / COD solubilisation of secondary sludge, and the methane production increased. The higher the temperature set for treatment, the higher the methane production was obtained. Thermal pre-treatments above 100°C are more effective compared to lower temperature (80°C). Thermal pre-treatment at 150°C increased the methane production by 58%, while 80°C pre-treated sludge only produced 10% more than non-treated sludge.
- Energy input is higher at higher temperature treatment. There is energy deficit from thermal treated secondary sludge after anaerobic digestion in this study. The heating efficiency of thermal pre-treatment needs to be improved, so that less energy is required.
- Electrolysis of secondary sludge showed promising results for improving secondary sludge anaerobic digestion. Both electrolysed sludge from anode

and cathode chamber produced 30% more methane gas than non-treated sludge.

- Effect of electrolysis is similar to that of chemical (acid, alkaline) pre-treatments. The electrolysis of sludge required less chemical addition (neutralize from pH 5 to 7) compared to alkaline or acid pre-treatments (neutralize from pH 2, 12).
- There is energy gain from the electrolysed secondary sludge, suggesting that this pre-treatment is energy efficient. However, the treatment duration is too long, thus need to be reduced.

4.2 Recommendations

The following are some further questions to be answered:

- The recycling rate of primary sludge at shorter HRT

  The experiment done in this study recycled almost 100% of the biomass back into the reactor to prevent methanogens washout. However, this is impossible in the actual industrial scale reactor, as the accumulated solids will exceed the volume capacity of the reactor. Therefore, further investigations are needed to determine the recycling rate for different days of HRT.
- Mixing intensity affects VFA degradation

  The experiment done in this study was not able to provide strong evidence if mixing intensity plays a part in the VFA accumulation. Therefore, further investigations are required.
- Better heating efficiency for thermal pre-treatment

  If better sludge heating system can be evaluated, the energy efficiency of thermal pre-treatment could be improved. The contact time of heating should be investigated as well, e.g. lower temperature may require longer contact time for effective results, whereas high temperature may only need short time for treatment.
- Further investigations for electrolysis pre-treatment is required:
  - Better pH gradient formation across anode and cathode electrode
  - Suitable material for anode and cathode chamber separation
  - Reduction of electrolysis time, increase efficiency

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Appendix

Energy input of electrolysis.

The current is calculated based on the voltage around the resistor,

I (Current) = V (volatage of resistor) / Resistance (5 Ω)

Energy (Watt) = VA * Time

For example,

At third hour, voltage of resistor = 0.204 V

Hence, Current = 0.204 V * 5Ω = 0.0408 A

Energy (watt) = V*A = 12 V * 0.0408 A (J s^{-1})

Energy (Joules) = 12 V* 0.0408 A*(ΔT) (J)

(where ΔT is the time difference from previous volatage measurement)

Energy = 12 V* 0.0408 A* 3*3600 s = 5287.68 J

The sum of energy consumed each time interval represents the energy input during the operation.

Table A. Raw data of voltage of resistor, current and energy input during electrolysis.

time (Hr)	Voltage of Resistor (V)	Resistance (Ω)	Current (amp)	Energy (W)
0				
3	0.204	5	0.0408	5287.68
4	0.203	5	0.0406	1753.92
5	0.196	5	0.0392	1693.44
6	0.195	5	0.039	1684.8
9.5	0.175	5	0.035	5292
10.5	0.169	5	0.0338	1460.16
11.5	0.173	5	0.0346	1494.72
12.5	0.169	5	0.0338	1460.16
13.5	0.162	5	0.0324	1399.68
14.5	0.154	5	0.0308	1330.56
23.5	0.121	5	0.0242	9408.96
27	0.114	5	0.0228	3447.36
30	0.104	5	0.0208	2695.68
			Total (800mL)	38409.12
			In 1 L	48011.4

The energy consumed in total equals 48011.4 joules = 48.01 kJ per liter of sludge